Promoter Effect of Chloride Ions on the Ruthenium-Catalyzed Hydroesterification of Ethylene with Methyl Formate. Design and Evaluation of New Poly- and Mononuclear Catalyst Precursors

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The catalytic hydroesterification of ethylene with methyl formate to produce methyl propionate is shown to take place in the presence of trinuclear ruthenium carbonyl complexes modified by anionic nucleophiles such as amido (anilinopyridyl), alkoxy (pyridonate), or halide ligands, regarded as potential promoters. The best results (100% conversion, 99% selectivity) are obtained with the mixture $Ru_3(CO)_{12} + [PPN]Cl(1/1)$ under the following experimental conditions: [HCOOMe]/[cat.] = 345, DMF solvent, $P(C_2H_4) = 20$ atm (at 25 °C), $\tilde{T} = 160$ °C, conditions: [HCOOMe]/[cat.] = 345, DMF solvent, $P(C_2H_4) = 20$ atm (at 25 °C), I = 160 °C, time = 12 h. The complex [PPN][Ru₃(μ_3 -Cl)(CO)₉] (3) resulting from the addition of [PPN]-Cl to Ru₃(CO)₁₂ reacts cleanly with an excess of [PPN]Cl in refluxing THF under a stream of inert gas to produce the unique dianionic species [PPN]₂[Ru₄(μ -Cl)₂(CO)₁₁] (4) (70% yield). The X-ray structure analysis of 4 is reported (triclinic $P\overline{1}$, No. 2, a = 18.209(2) Å, b = 18.877-(3) Å, c = 13.895(2) Å, $\alpha = 110.70(1)^{\circ}$, $\beta = 108.43(1)^{\circ}$, $\gamma = 87.43(1)^{\circ}$, V = 4226(1) Å³, Z = 2, R = 0.053, $R_w = 0.069$). The dianionic tetranuclear unit of 4 consists of a basic triangular metal framework "Ru₃(CO)₉" one face of which is supported by a spiked "Ru(CO)₂Cl₂" fragment involving a 16e metal center exhibiting a square pyramidal geometry. Extended fragment involving a 16e metal center exhibiting a square pyramidal geometry. Extended Hückel MO calculations indicate a large HOMO/LUMO gap (1.45 eV). Facile loss of Clfrom the above dianion is induced by capture of CO, leading to the known butterfly complex [PPN][Ru₄(μ -Cl)(CO)₁₃] (5). Complex 4 also reacts with O₂ at 25 °C to provide the new oxo derivative $[PPN]_2[Ru_4(\mu_4-O)(\mu-Cl)_4(CO)_{10}]$ (6). The structure of 6 has been determined by X-ray diffraction (triclinic P1, No. 2, a = 13.226(5) Å, b = 25.533(2) Å, c = 12.771(3) Å, $a = 92.39(1)^\circ$, $\beta = 114.77(3)^\circ$, $\gamma = 85.92(2)^\circ$, V = 3906(2) Å³, Z = 2, R = 0.038, $R_w = 0.045$). Its dianionic unit consists of a distorted quadratic antiprism based on two rectangular faces $Ru(\mu-Cl)_2Ru$ and containing an encapsulated oxygen atom linked to the four ruthenium centers. The anionic complexes 4-6 also act as catalyst precursors for the hydroesterification reaction. Analysis of the solutions recovered at the end of all catalytic runs indicate the presence of $[PPN]_2[Ru_6(C)(CO)_{16}]$ as the principal metal-containing derivative. The probable mononuclear nature of the active species is suggested. A detailed investigation of the catalytic system based on [PPN][Ru(\overline{CO})₃Cl₃] (7) (prepared here in 81% yield by a new onepot procedure) is reported. The results show that catalysis in the presence of the latter complex takes place readily without an induction period. Furthermore, a comparative evaluation of the four salts 7, [PPN][Ru(CO)₃I₃] (8), [PPN][Ru(CO)₃Cl₂I] (9), and [PPN][Ru(CO)₃-ClI₂] (10) as catalyst precursors reveals that chloride is a better promoter than iodide under the experimental conditions defined above, using DMF (or related amides) as solvent. Catalysis in the presence of 7 (and 3 equiv of NEt₃ as cocatalyst) is complete within 2 h (100% conversion and 99% selectivity; overall turnover frequency = 170 h⁻¹, corresponding to an initial activity of the order of 700 h⁻¹). Complex **7** is seen to react readily with DMF at 160 °C within 30 min to produce the new complex [PPN][Ru(CO)₂Cl₃(η^1 -DMF)] (11), isolated in 60% yield. The X-ray structure of 11 is reported (monoclinic $P2_1/c$, a = 9.000(2) Å, b = 21.176(2) Å, c = 21.080(1) Å, $\beta = 93.89(8)^\circ$, V = 4008.3(9) Å³, Z = 4, R = 0.028, $R_w = 0.030$). The three chloride ligands adopt a meridional arrangement, whereas the DMF ligand, bound via its oxygen atom, occupies one of the two apical sites.

Introduction

Methyl formate is a valuable feedstock in organic synthesis,^{1,2} and its "direct" addition to olefins for the

production of esters is of potential industrial importance.³ The homogeneous catalytic hydroesterification of ethylene with methyl formate was originally discov-

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Table 1. Performances of the Principal Ru-Based Catalytic Systems for the Hydroesterification of Ethylene with Methyl Formate (Selected Results)

author	precursor	solvent	conditions	activity (h ⁻¹)	ref
Sneeden et al.	RuCl ₂ (PPh ₃) ₃	methyl	190 °C	16	4
		formate	20 atm		
			18 h		
Ueda et al.	$RuH_2(PPh_3)_4$	THF	90 °C	а	7
			40 atm		
			23 h		
Keim et al.	$Ru_3(CO)_{12}$	toluene	230 °C	230	8
			90 atm		
			20 h		
Keim et al.	$[Ru_3(CO)_{10}Cl]^-$	toluene	230 °C	50	8
			90 atm		
			20 h		
Petit et al.	RuCl ₃ /2 [Et ₄ N]]	DMF	190 °C	1450 ^b	11
	· · · · ·		55 atm		
			1 h		

" Data not available; the reported [product]/[formate] ratio was 5.4. b Typical value taken from the patent; 11b such a value, measured at 65% conversion, is not directly comparable with Keim's results.8

ered by Sneeden and co-workers in 1983, using RuCl₂-(PPh₃)₃ at 190 °C (Table 1).⁴ A Pd-based process at room temperature was then patented by Alper and co-workers.^{5,6} More recently, a number of modified Ru-based catalytic systems were also developed by several authors.⁷⁻¹¹ In particular, Keim and Becker⁸ reported that Ru₃(CO)₁₂ functions as a catalyst precursor notably superior to the chloride-containing complex [PPN][Ru₃- $(\mu$ -Cl)(CO)₁₀]. Finally, a highly efficient catalytic procedure based on RuCl₃·nH₂O/[Et₄N]I was patented by the late Professor Petit and his co-workers.¹¹

An apparent negative influence of the chloride ion was noted by Keim,⁸ at a working temperature of 230 °C. This was in sharp contrast to the booster effect of iodide in the patented process at 190 °C.¹¹

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With the aim to rationalize these discrepancies, we set out to evaluate the relative efficiency of a range of anionic nucleophiles as promoters for the hydroesterification reaction using $Ru_3(CO)_{12}$ as a catalyst precursor. The coordinating anions selected for this study included halides,^{12,13} as well as specific alkoxide, amide, and thiolate groups which were prone to function as hemilabile ligands.^{14,15} Indeed, in light of earlier findings, it might be anticipated that a stepwise introduction of ethylene and methyl formate in the coordination sphere of the cluster would be facilitated by bridge-opening reactions of the type encountered in the equilibria involving either [PPN][Ru₃(Cl)(CO)_{12-n}] $(n = 1-3)^{12,13}$ or [PPN][Ru₃(μ -(C₆H₅)N(C₅H₄N))(CO)_{12-n}] (n = 2, 3) (Scheme 1).^{14,15} Kinetic data on such bridge-opening processes have now been obtained by Basolo and coworkers.¹⁶

We were obviously prepared to consider the alternate possibility that the above polymetallic species might act as sources of active mononuclear fragments generated in situ under catalytic conditions.

In a preliminary screening, triruthenium carbonyl complexes incorporating the above mentioned ancillary ligands were tested as catalyst precursors. Analysis of the results led us to a thorough investigation of the ruthenium/chloride system, found to be the most active in amide solvents under the specific conditions defined below. An unexpected outgrowth of this work was the discovery of new dianionic polymetallic ruthenium carbonyl halide complexes resulting from the incorporation of more than one chloride ligand into $Ru_3(CO)_{12}$. The unprecedented odd structures of these compounds are rationalized in terms of EHMO calculations. The observation that such polymetallic species are transformed under catalytic conditions led us to evaluate mononuclear complexes as alternate catalyst precursors. In particular, [PPN][Ru(CO)₃Cl₃] was found to be highly efficient, achieving the hydroesterification of ethylene under milder conditions than with other Ru-based catalytic systems. The latter complex reacts with the dimethylformamide solvent under catalytic conditions to give the new species [PPN][Ru(CO)₂Cl₃(η^1 -OCHN-

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 Table 2. Preliminary Screening of Various Catalyst Precursors^a

entry	catalyst precursor	solvent	conv (%)	selec (%)
1	$Ru_3(\mu-H)(\mu-PhNPy)(CO)_9$	THF	0	0
2	$[PPN][Ru_3(\mu-PhNPy)(CO)_9]$	THF	28	77
3	$[PPN][Ru_3(\mu-PhNPy)(CO)_9]$	DMF	33	96
4	$[PPN][Ru_3(\mu - OPy)(CO)_{10}]$	THF	40	78
5	[PPN][Ru ₃ (μ -OPy)(CO) ₁₀]	DMF	58	88
6	$[PPN][Ru_3(\mu-SPy)(CO)_9]$	THF	0	0
7	$[PPN][Ru_3(\mu-Cl)(CO)_{10}]$	THF	2	93
8	[PPN][Ru ₃ (µ-Cl)(CO) ₁₀]	DMF	100	99

^{*a*} Experimental conditions: Catalyst precursor (0.235 mmol), HCO₂CH₃ (5 mL), [formate]/[cat.] = 345, solvent (15 mL), $P(C_2H_4) = 20$ atm, T = 160 °C, reaction time = 12 h.

 $(CH_3)_2)]. \ A preliminary account of part of this work has been published. <math display="inline">^{17}$

Results

A. Design and Evaluation of Polynuclear Catalyst Precursors. Preliminary screening of Various **Promoters.** Preliminary catalytic runs were first carried out in THF solution under the typical experimental conditions defined in Table 2 (entries 1, 2, 4, 6, 7). The catalyst precursors were preformed triruthenium carbonyl complexes incorporating various ancillary ligands regarded as potential promoters. Though the neutral hydrido species $\operatorname{Ru}_3(\mu-H)\{\mu-(C_6H_5)N(C_5H_4N)\}(CO)_9$ involving an anilinopyridyl group as a ligand was totally inefficient (entry 1), the corresponding deprotonated anionic species [PPN][$Ru_3\{\mu - (C_6H_5)N(C_5H_4N)\}(CO)_9$] was found to exhibitit a moderate activity. Even better results were obtained with the complex [PPN][Ru₃{ μ - $O(C_5H_4N)$ (CO)₁₀] bearing an alkoxypyridyl group as the ancillary ligand. Noticeably, no activity was observed in the presence of $[PPN][Ru_3\{\mu-S(C_5H_4N)\}(CO)_9]$.

It is noteworthy that the chloride complex [PPN][Ru₃- $(\mu$ -Cl)(CO)₁₀] generated *in situ* from Ru₃(CO)₁₂ and [PPN]Cl had no promoter effect in THF solvent (entry 7).

A recurrent observation was that, regardless of the nature of the anionic promoter, the red solutions recovered at the end of catalytic runs were all roughly

Table 3. Efficiency of Various Salts as Promoters for theHydroesterification Reaction Based on Ru3(CO)12 as aCatalyst Precursor in DMF Solvent^a

entry	promoter	conversion (%)	selec (%)	turnover
1	none	30	96	101
2	KI	56	91	182
3	[PPN]I	66	97	264
4	[NBu₄]F	74	87	223
5	NaCl	59	98	203
6	[PPN]Cl	100	99	339

"Experimental conditions: Ru₃(CO)₁₂ (0.235 mmol), promoter (0.235 mmol), HCO₂CH₃ (5 mL) ([formate]/[cat.] = 345), DMF (15 mL), $P(C_2H_4)$ = 20 atm, T = 160 °C, reaction time = 12 h.

exhibiting the same infrared spectrum in the $\nu(CO)$ region. The corresponding species was subsequently identified as $[PPN]_2[Ru_6C(CO)_{16}]$ (vide infra).

In the pioneering work of Sneeden and co-workers on the hydroesterification of ethylene (originally using methyl formate as solvent),⁴ it was noted that the presence of amide solvents such as *N*-methylpyrrolidone (NMP) or dimethylformamide (DMF) accelerates the decomposition of methyl formate, with production of CO. Using RuCl₃nH₂O in NMP/toluene mixtures, these authors observed for the first time good selectivities in methyl propionate. More recently, DMF proved to be essential as solvent for the mixture RuCl₃nH₂O + 2-[NEt₄]I used by Petit and co-workers in their patented hydroesterification process.¹¹

Under our experimental conditions, the activity of most doped catalyst precursors was also dramatically enhanced by the use of DMF (Table 2, entries 3, 5, 8). Surprisingly, the complex [PPN][Ru₃(μ -Cl)(CO)₁₀] which had been found inefficient in THF, became highly active in DMF, achieving 100% conversion and 99% selectivity!

This led us to evaluate the relative efficiency of various halide salts as promoters for the hydroesterification reaction in DMF solvent. Experiments reported in Table 3 revealed that (i) onium salts are better promoters than alkaline salts, and (ii) the chloride ion is superior to other halides. Considering these results, we set out to examine in detail the system based on $Ru_3(CO)_{12}$ as a catalyst precursor and [PPN]Cl as a promoter, using DMF as solvent.

As shown in Table 4, the optimum temperature for the $Ru_3(CO)_{12}/[PPN]Cl$ system was found to be 160 °C.

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Table 4. Temperature Optimization for the System Using $Ru_3(CO)_{12}$ + [PPN]Cl as Catalyst Precursor in DMF Solvent^a

entry	T (°C)	conv (%)	selec (%)	turnover
1	130	5	95	17
2	150	74	98	255
3	160	100	99	339
4	170	100	35	122
5	180	100	28	99

^a Experimental conditions: Ru₃(CO)₁₂ (0.235 mmol), [PPN]Cl (0.235 mmol), HCO₂CH₃ (5 mL) ([formate]/[cat.] = 345), DMF (15 mL), $P(C_2H_4)$ = 20 atm, reaction time = 12 h.

Loss of selectivity in methyl propionate, with concomitant formation of methanol and CO, was observed as the temperature was raised above 180 °C.

In summary, at the end of the above preliminary study, the optimum conditions were those summarized below in eq 1. Noticeably, no attempts were made to optimize the reaction time of these preliminary experiments which were all carried out overnight.

99% selectivity

Reaction of [PPN][$Ru_3(\mu_3-Cl)(CO)_9$] with an excess of halide ions. Formation of $[PPN]_2[Ru_4(\mu Cl_2(CO)_{11}$]. During the course of preliminary experiments aimed at evaluating the optimum Ru/halide ratio, we noted that when THF solutions of [PPN][Ru₃(μ_3 -Cl)- $(CO)_{9}$ (3) were refluxed under an argon stream in the presence of an excess of [PPN]Cl, a characteristic blood red crystalline precipitate was progressively appearing over a period of 1 h. This new air sensitive complex was recovered in 70% yield after recrystallization from dichloromethane/hexane solutions. It was subsequently formulated as $[PPN]_2[Ru_4(\mu-Cl)_2(CO)_{11}]$ (4) on the basis of an X-ray structure analysis (vide infra). The overall stoichiometry of the reaction corresponds to eq 2.

 $4[PPN][Ru_{3}(\mu_{3}\text{-}Cl)(CO)_{9}] + 2[PPN]Cl \xrightarrow[THF, 66 °C, 1 h]{argon stream}$ $3[PPN]_{2}[Ru_{4}(\mu-Cl)_{2}(CO)_{11}] + 3CO$ (2)

The structure of the dianionic cluster unit is represented here in a simplified structural drawing, whereas an ORTEP diagram is also provided in Figure 1.





Figure 1. Perspective view of the dianionic unit of complex 4. For clarity purposes, the labels of carbonyl groups are shown only at oxygen atoms.

This exotic architecture provides the image of a mononuclear unsaturated complex $[Ru(CO)_2Cl_2]^{2-}$ that would be anchored onto the surface of a basic triangular cluster unit "Ru₃(CO)₉". Indeed, the ruthenium center Ru(4) and its two neighboring halide atoms are respectively "spiked" on the three axial coordination sites of the basic trimetallic unit. Furthermore, the mean plane of the " $Ru(CO)_2Cl_2$ " unit is roughly parallel to the plane of the triangular support (the dihedral angle is $4.8(1)^{\circ}$). The most striking feature is indeed the occurrence of a square pyramidal geometry about the 16e metal center Ru(4) (regarding Ru(3) as the "apical" atom). In the rare cases of mononuclear complexes where such a geometry is found,¹⁸⁻²⁰ the vacant octahedral site is generally protected by an agostic interaction.²¹ For example, in $RuCl_2(PPh_3)_3$, one of the phenyl groups of a triphenylphosphine ligand interacts directly with the metal through one of its H atoms (Ru···H = 2.59 Å).¹⁹ In complex 4, the shortest intermolecular contact involves Ru(4) and an H atom which belongs to one of the phenyl rings of a PPN cation ($\operatorname{Ru}(4) \cdot \cdot \cdot \operatorname{H}(53) = 2.919(9) \text{ Å}$). The latter value is unusually short for a simple van der Waals contact. Furthermore, the exact geometrical location of H(53) on the "vacant" octahedral coordination site tends to indicate the occurrence a weak interaction which may be assimilated to an agostic interaction and is apparently sufficient to stabilize the coordinative unsaturation.

Extended Hückel molecular orbital calculations^{22,23} were carried out on 4, with an idealized averaged structure of C_s symmetry (see Experimental Section). Its MO diagram (Figure 2) is based on the interaction between the respective fragments $Ru_3(CO)_9\ (left)$ and $[Ru(CO)_2Cl_2]^{2-}$ (right).

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Figure 2. Interaction MO diagram for compound 4, assuming an idealized structure of C_s symmetry.

The $[Ru(CO)_2Cl_2]^{2-}$ moiety exhibits the usual electronic structure of stable 16-electron square planar species, with a large HOMO/LUMO gap separating the four nonbonding occupied d-type orbitals from the z-type LUMO. The electron deficiency of the 42-electron "Ru₃(CO)₉" fragment is illustrated by the presence of three empty acceptor orbitals lying in the -11 to -10eV energy range (3a', 4a', and 2a"). The main bonding interactions between the two fragments involve the three acceptor orbitals of " $Ru_3(CO)_9$ " on one side and the z²-type HOMO (3a') and chlorine-localized occupied orbitals of $[Ru(CO)_2Cl_2]^{2-}$ on the other side. These latter low-lying levels are not shown in Figure 2. The computed overlap population is 0.644, and the total charge transfer from $[Ru(CO)_2Cl_2]^{2-}$ to $Ru_3(CO)_9$ is 0.9 electron, of which ca. 0.32 come from Ru(4). There is

almost no π -electron transfer between the fragments. The main bonding interaction between Ru(4) and the $Ru_3(CO)_9$ moiety occurs between the z²-type 3a' HOMO of $[Ru(CO)_2Cl_2]^{2-}$ and the 3a' LUMO of $Ru_3(CO)_9$. The HOMO (5a')/LUMO (6a') gap of 4 is rather large (1.45 eV), indicating a good thermodynamical stability. The HOMO, which is mainly localized on the triangular Ru₃- $(CO)_9$ entity (90%) is the out-of-phase component resulting from the 4-electron-two-orbital destabilizing interaction of the metallic 2a' MO of $Ru_3(CO)_9$ with the 1a'(xz) MO of $[Ru(CO)_2Cl_2]^{2-}$. The LUMO is the nonbonding combination deriving from the interaction of the metallic 4a' level of $Ru_3(CO)_9$ on one side, with the upper 4a' (z) and the lower 3a' (z^2) orbitals of [Ru(CO)₂Cl₂]²⁻ on the other side. The participation of $Ru(CO)_2Cl_2$ in this LUMO is fairly large (44%, of which 26% is coming

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from Ru(4)). The overlap populations computed between the metal atoms are 0.133, 0.141, and 0.146 for the Ru(1)-Ru(2), Ru(1,2)-Ru(3), and Ru(3)-Ru(4) contacts, respectively. They reflect the differences observed in the metal-metal distances. The Ru(1,2)-Cl overlap populations are rather important and comparable to that found for Ru(4)-Cl (0.278 vs 0.337, respectively).

Thus, this orbital analysis supports our view of compound 4 as a saturated 48e triruthenium system bearing a mononuclear 16e square pyramidal metal fragment on one face. Although unprecedented in cluster chemistry, the square pyramidal arrangement around Ru(4) is not uncommon for 16e mononuclear species. Theoretical calculations by El Idrissi *et al.*¹⁸ have shown that such a geometry is favored for d⁶ ML₅ species having strong σ -donor ligands *trans* to the vacant octahedral site. This is obviously the case here, where a strong σ -type interaction exists between Ru(4) and Ru(1) (vide supra). The same authors have shown that the alternative trigonal bipyramidal structure is Jahn-Taller unstable.¹⁸ Our calculations on the tentative alternate theoretical model 4' exhibiting such a



geometry indicate that the trigonal bipyramidal structure exhibits a triplet ground state and requires two electrons more to achieve a closed shell configuration, with a HOMO/LUMO gap of 1.03 eV. Thus, 4' is less stable than 4 by almost 2 eV, with a very small Ru(3)-Ru(4) overlap population (0.036).

Calculations aimed at evaluating the acceptor capabilities of 4 were also performed: hypothetical introduction of a hydride ligand on the vacant coordination site of Ru(4), at a distance of 2.0 Å from the metal, resulted in a Ru(4)-H overlap population of 0.293. When the same calculations were made after replacement of the "Ru₃(CO)₉" unit by strong σ -donors such as CH₃⁻ or PH₃, the corresponding overlap populations became 0.346 and 0.366, respectively. These results suggest that the metal atom Ru(4) in 4 is a strong electrophilic center, although probably weaker than a 16-electron Ru^{II}L₅ mononuclear species.

An energy gap of 0.51 eV separates the 5a' HOMO of 4 from its next occupied 4a' neighbor orbital. Since the former is slightly $Ru_3(CO)_9-Ru(CO)_2Cl_2$ antibonding, its depopulation should lead to some shortening of the Ru-(3)-Ru(4) distance. Unfortunately, this cannot be verified experimentally since the compound does not give a simple oxidized product.

As expected due to its unsaturation, the compound was found to be highly reactive. However, to date, we have been unable to intercept any adduct resulting from simple capture of the vacant coordination site by an incoming nucleophile. In fact, addition of donor ligands triggers further rearrangements of this rather unstable polymetallic architecture. Typically, reaction with CO takes place almost instantaneously at 25 °C and induces concomitant loss of one halide to give the known thermodynamically stable butterfly compound [PPN]-[Ru₄(μ -Cl)(CO)₁₃] (5) (eq 3).²⁴



The reverse reaction takes place quantitatively in refluxing THF over a period of 90 min.

Oxygenation of $[PPN]_2[Ru_4(\mu-Cl)_2(CO)_{11}]$ and formation of $[PPN]_2[Ru_4(\mu_4-O)(\mu-Cl)_4(CO)_{10}]$. Solutions of complex 4 rapidly turn yellow upon adventitious exposure to air, leading to a new compound obtained as bright yellow crystals. The new complex was formulated as $[PPN]_2[Ru_4(\mu_4-O)(\mu-Cl)_4(CO)_{10}]$ (6) on the basis of an X-ray structure analysis.



Complex **6** is a new member of the family of polymetallic oxo compounds.²⁵ The structure of its dianionic molecular unit is represented in both the simplified drawing shown here and a perspective view displayed in Figure 3.

The molecule appears as a cage built around a central oxygen atom exhibiting a distorted tetrahedral (sp^3) geometry. The cage defined by Ru and Cl atoms is a slightly distorted quadratic antiprism (noncrystallographic D_2 symmetry) based on two rectangular faces $Ru(\mu-Cl)_2Ru$. The unique oxygen is linked to four equivalent ruthenium centers. Each metal atom is surrounded by six ligands, namely, the central oxygen atom, three carbonyl groups (one bridging, two terminal), and two chloride atoms. The latter chloride ligands are in asymmetric bridging positions between two metal centers, in such a way that the coordination sphere of each metal center involves both a short (average value,

⁽²⁴⁾ Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L. Inorg. Chem. 1980, 19, 2985.

<sup>1980, 19, 2985.
(25) (</sup>a) For a review on polymetallic oxo compounds, see: Bottomley,
F.; Sutin, L. Adv. Organomet. Chem. 1988, 28, 339 and references therein. (b) Schleid, T.; Meyer, G. J. Less-Common Met. 1987, 127, 161. (c) Cotton, F. A.; Hong, B.; Shang, M. Inorg. Chem. 1993, 32, 4876.
(d) Schauer, C. K.; Shriver, D. F. Angew. Chem., Int. Ed. Engl. 1987, 26, 255. (e) Schauer, C. K.; Voss, E. J.; Sabat, M.; Shriver, D. F. J. Am. Chem. Soc. 1989, 111, 7662.



Figure 3. Perspective view of the dianionic unit of complex **6.** For clarity purposes, the labels of carbonyl groups are shown only at oxygen atoms.

2.461 Å) and a long (average value, 2.716 Å) Ru-Cl interaction. The chlorine atom which is the less strongly bound to the ruthenium center is the ligand which is the furthest away from the ideal octahedral site. Such a distortion can be attributed to steric repulsions between the chloride atoms within the double bridge, as suggested by the occurrence of rather short nonbonding contacts (Cl(1) · · Cl(3) = 3.35 Å; Cl(2) · · Cl(4) = 3.32 Å). In summary, the four metal atoms constitute a tetrahedron, the edges of which can be divided in three groups of two. The largest Ru-Ru separations (ca. 3.8 Å) correspond to the unbridged edges of the tetrahedron. The intermediate separations (ca. 3.2 Å) correspond to the Separations (ca. 3.1 Å).

The molecule can be described as an ensemble of four hexacoordinated ruthenium centers linked together through a unique oxo ligand. This simple picture is supported by EHMO calculations based on the experimental molecular structure. The large value of the calculated HOMO/LUMO gap (2.13 eV) is much more characteristic of a mononuclear ruthenium species rather than a compound presenting significant metalmetal interactions. Over the range -11.8 to -12.8 eV, the 14 highest occupied levels constitute a group being well isolated on the energy scale. This block is made from the 4×3 "t_{2g}" levels of the four independent metal centers mixed with two bonding MOs deriving from the two bridging carbonyls. The other occupied levels, predominantly ligands in character, lie below -14 eV.

The fact that the corresponding overlap populations between the metals are all slightly negative (average value = -0.023) indicates weak repulsive interactions and, hence, absence of Ru-Ru bonding. The strongest repulsions correspond to the shortest, CO-bridged Ru···Ru separations (-0.039 and -0.036 for Ru(1)···Ru-(2) and Ru(3)···Ru(4), respectively). Repulsive interactions are also present between the chlorine atoms which are bridging the same metal-metal vector, as expected from the molecular structure (see above). The corresponding overlap populations are -0.010 and -0.011for Cl(1)···Cl(3) and Cl(2)···Cl(4), respectively. The Ru-O and Ru-Cl (short bond) overlap populations

Table 5. Performances of Various Mono- and DianionicPolymetallic Ruthenium Carbonyl Halide Complexes Used asCatalyst Precursors^a

entry	catalyst precursor	[substr]/ [cat.]	conv (%)	selec (%)	turnover
1	$Ru_3(CO)_{12} + [PPN]Cl$	345	100	99	339
2	$[PPN][Ru_4(\mu-Cl)(CO)_{13}]$	345	100	99	339
3	$[PPN]_{2}[Ru_{4}(\mu-Cl)_{2}(CO)_{11}]$	405	95	98	381
4	$[PPN]_2[Ru_4(\mu-Cl)_4(\mu_4-O)(CO)_{10}]$	405	88	97	345
5	$[PPN]_2[Ru_6C(CO)_{16}]$	901	53	44	207

" Experimental conditions: HCO_2CH_3 (5 mL), DMF (15 mL), $P(C_2H_4) = 20$ atm, T = 160 °C, reaction time = 12 h.

exhibit values of 0.234 and 0.308, respectively, thereby indicating substantial metal-ligand bonding, whereas the corresponding average value of 0.157 for the long Ru-Cl bonds indicates significantly weaker interactions. This suggests that a partial decoordination of one or several chlorine ligands should be possible in solution at reasonable temperatures, generating reactive coordination sites on one or several atoms.

Evaluation of the New Complexes as Catalyst Precursors. Identification of the Principal Metal-Containing Species at the End of Catalytic Runs. Following the isolation and characterization of the above dianionic species, we attempted to evaluate their efficiency as catalyst precursors (Table 5). It appeared that the performances obtained with $[PPN]_2[Ru_4(\mu-Cl)_2 (CO)_{11}$ (4), [PPN][Ru₄(μ -Cl)(CO)₁₃] (5), or [PPN]₂[Ru₄- $(\mu_4-O)(\mu-Cl)_4(CO)_{10}$] (6) matched those obtained with $Ru_3(CO)_{12} + [PPN]Cl$. The fact that complexes exhibiting rather different structures had roughly the same efficiencies was interpreted as a strong indication that they were just acting as the precursors to the same active species. Furthermore, it appeared that the solutions recovered at the end of all catalytic runs exhibited the same infrared pattern in the $\nu(CO)$ region, regardless of the nature of the anionic precursor. The species responsible for the observed infrared pattern was isolated from the solution, crystallized, and unambiguously identified as the known dianionic carbido complex [PPN]₂[Ru₆(C)(CO)₁₆].²⁶ However, only moderate performances (Table 5, entry 5) were recorded when the complex was used as a catalyst precursor, thereby indicating that it was not the active species, but an end product resulting from its decomposition.

Interestingly, $[PPN]_2[Ru_6(C)(CO)_{16}]$ had been also isolated earlier by Dombek as a residual product in a related catalytic system, namely, the rutheniumcatalyzed syngas conversion to ethylene glycol, using KI as a promoter.²⁷ With this in mind, we reasoned that the two catalytic systems might possibly involve the same active species at the intermediate stage. In the glycol synthesis, the active species generated *in situ* upon reaction of Ru₃(CO)₁₂ with KI under hydrogen pressure had been proposed to be a mixture of [Ru₃(μ -H)(CO)₁₁]⁻ and [Ru(CO)₃I₃]⁻²⁷ Though molecular hydrogen was not involved in our system, hydrido com-

^{(26) (}a) This carbido complex had been originally obtained upon reaction of $Ru_3(CO)_{12}$ with ethylene in the presence of a base.^{26b.c} (b) Bradley, J. S.; Ansell, G. B.; Hill, E. W. J. Organomet. Chem. **1980**, 184, C33-C35. (c) Johnson, B. F. G.; Lewis, J.; Sankey, S. W.; Wong, K.; McPartlin, M.; Nelson, W. J. H. J. Organomet. Chem. **1980**, 191, C3-C7.

^{(27) (}a) Dombek, B. D. J. Am. Chem. Soc. 1981, 103, 6508. (b)
Dombek, B. D. J. Organomet. Chem. 1983, 250, 467. (c) Dombek, B.
D. Organometallics 1985, 4, 1707. (d) Dombek, B. D. J. Organomet. Chem. 1989, 372, 151 and references therein.

Table 6. Evidence for the Efficiency of [PPN][Ru(CO)₃Cl₃]^a

entry	catalyst precursor	time (h)	conv (%)	selec (%)	TOF (h^{-1})
1	[HRu ₃ (CO) ₁₁] ⁻	12	100	25	8
2	$[Ru(CO)_{3}Cl_{3}]^{-} + 2 [HRu_{3}(CO)_{11}]^{-}$	3	72	98	83
3	$[Ru(CO)_3Cl_3]^-$	3	80	95	89

" Experimental conditions: entry 1, [PPN][HRu3(CO)11] (0.235 mmol); entry 2, [PPN][Ru(CO)₃Cl₃] (0.235 mmol), [PPN][HRu₃(CO)₁₁] (0.470 mmol); entry 3, [PPN][Ru(CO)₃Cl₃] (0.235 mmol); HCO₂CH₃ (5 mL), DMF (15 mL), $P(C_2H_4) = 20$ atm, T = 160 °C.

plexes might have been generated in situ from ethylene or methyl formate under catalytic conditions. Thus, the activity of the mixture $[Ru_3(\mu-H)(CO)_{11}]^- + [Ru(CO)_3X_3]^$ was evaluated in the formate/ethylene reaction, keeping in mind that such a mixture had been also found active in a conventional hydroalkoxycarbonylation process using $CO + MeOH^{28}$ Whereas the results were still found totally negative when X was the iodide ligand, the use of the chloride-containing salt resulted in a spectacular rate enhancement and completion of the reaction within 3h (Table 6, entry 2). Finally, the salt $[PPN][Ru(CO)_3Cl_3]$ alone (entry 3) was found as active as the mixture [PPN][Ru(CO)₃Cl₃] + 2[PPN][Ru₃(μ -H)- $(CO)_{11}$, which ruled out a participation of the latter salt in the present case.

The advantage of using [PPN][Ru(CO)₃Cl₃] instead of the Ru₃(CO)₁₂/[PPN]Cl mixture is illustrated by the diagram showing the respective evolution of the internal pressure as a function of time for the two systems (Figure 4): whereas the reaction initiated with the mixture Ru₃(CO)₁₂/[PPN]Cl starts only after an induction period of ca. 3 h, catalytic reaction takes place rapidly in the presence of $[PPN][Ru(CO)_3Cl_3]$. Thus, the mononuclear complex appears to be much closer to the active species than the former cluster. One may reasonably suggest that the induction period required to activate the cluster corresponds to the generation of active fragments of lower nuclearity. Even though slightly lower conversion rates and selectivities were obtained from the initial catalytic runs where the mononuclear complex was used as a precursor, we next found that the addition of an excess of [PPN]Cl (1 equiv) to the mononuclear complex [PPN][Ru(CO)₃Cl₃] allows us to match the performances obtained with the cluster, namely, 97% conversion and 98% selectivity, within a much shorter reaction time (vide infra). In view of further developments of a catalytic system based on the mononuclear precursor, it was first necessary to improve the yield of its preparation.

B. Design and Evaluation of Mononuclear Catalyst Precursors. "One Pot" Synthesis of [PPN][Ru- $(CO)_3Cl_3$]. The complex [PPN][Ru(CO)_3Cl_3] can be readily obtained by treatment of the dimer $[Ru(CO)_3 Cl_2]_2$ with [PPN]Cl in parallel with the procedure reported for iodide salts.²⁹ However, the published multistep procedure for the preparation of the antecedent bimetallic species $[Ru(CO)_3Cl_2]_2$ is not convenient for extensive use since it necessitates, first, the preparation of $Ru_3(CO)_{12}$ from the commercial ruthenium trichloride RuCl₃·3H₂O,³⁰ and then the reintroduction

of chloride ions via reaction with HCCl₃ in a reactor.³¹ The corresponding overall yield of $[PPN][Ru(CO)_3Cl_3]$ never exceeds 28%, due to cumulated losses along the four individual steps.

While routinely preparing samples of Ru₃(CO)₁₂ via the method reported by Mantovani and Cenini,³⁰ namely, the two-step reduction of RuCl₃, nH₂O by CO and zinc, we were intrigued by slight variations in the color of the intermediate yellow solution obtained at the end of the first reduction step. Such variations occurred when the solution was kept overnight under CO at room temperature. We realized that the exact composition of this mixture (referred to as "lemon-yellow solution" in the published procedure³⁰) had never been determined before. A careful monitoring by infrared spectroscopy allowed us to identify the principal species present in this mixture (Scheme 2). Typically, when $RuCl_3 nH_2O$ was refluxed in ethoxyethanol under a fast stream of carbon monoxide, a color change from dark brown to blood red was observed after 20 min. At that stage, the IR spectrum exhibited two bands of equal intensity at 2060 and 1990 cm^{-1} that could be attributed to the polymeric complex $[Ru(CO)_2Cl_2]_n$ (though it has been suggested that the latter species might be trimeric, its structure has in fact never been established).32 While the red color progressively turned yellow under prolonged reaction with CO, an additional band appeared at 2125 cm⁻¹, whereas the 2060 cm⁻¹ band was simultaneously enlarged and slightly shifted down to 2056 cm^{-1} . Such a spectral change was ascribed to the progressive formation of the dimeric complex [Ru- $(CO)_{3}Cl_{2}]_{2}$ (2125 (s), 2050 (vs) cm⁻¹) at the expense of the polymeric species.³³ The complete transformation of the polymeric species into the colorless dimer was achieved upon prolonged treatment with CO for ca. 7 h at room temperature. Alternately, such a transformation could be more readily achieved under CO pressure (10 atm, 80 °C, 1 h). The dimeric compound [Ru- $(CO)_{3}Cl_{2}]_{2}$ was recovered by evaporation of the solvent and then dissolved in THF. Further addition of [PPN]-Cl allowed precipitation of the salt $[PPN][Ru(CO)_3Cl_3]$. After recrystallization from methanol, the overall yield of [PPN][Ru(CO)₃Cl₃] relative to the starting material RuCl₃·nH₂O was 81% (Scheme 2).

An X-ray structure analysis of the crystals confirmed that the compound is obtained as the *fac*-isomer, as established earlier from a structural analysis of the salt $[H_5O_2][Ru(CO)_3Cl_3]$ ·SbCl₃.³⁴

Synthesis of [PPN][$Ru(CO)_3X_nX'_{3-n}$] (X = Cl, X' = I, n = 1, 2). Whereas [PPN][Ru(CO)₃Br₃] was prepared by adaptation of the procedure published for [PPN][Ru(CO)₃I₃],²⁹ we needed samples of mixed chloride/ iodide salts in order to evaluate the respective efficiency of these halide ions as promoters (vide infra). The salt [PPN][Ru(CO)₃Cl₂I] was prepared by simple reaction of the chloride dimer [Ru(CO)₃Cl₂]₂ with [PPN]I, whereas [PPN][Ru(CO)₃ClI₂] was obtained by reacting [Ru(CO)₃I₂]₂ with [PPN]Cl.

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⁽³⁴⁾ Teulon, P.; Roziere, J. Z. Anorg. Allg. Chem. 1981, 483, 219.



Figure 4. Comparative study of the relative efficiency of polynuclear and mononuclear ruthenium carbonyl chloride complexes as catalyst precursors under the experimental conditions defined in Table 6. The plots represent the evolution of the internal pressure within the reactor as a function of time.

Scheme 2



Optimization of the Catalytic System Based on [PPN][Ru(CO)₃Cl₃]. Influence of the Temperature. The results of catalytic runs performed at various temperatures are reported in Table 7, whereas the corresponding graph tracing the evolution of the internal pressure as a function of time is displayed in Figure 5. The optimum activity was obtained at 180 °C. Interestingly, the plot corresponding to the catalytic run performed at 200 °C clearly showed a fast decrease of the ethylene pressure in the initial stage, followed after 10 min by a sudden pressure increase consistent with a decomposition of methyl formate into methanol and CO. It is noteworthy that, even though all the required substrates (MeOH + CO) necessary for a conventional

 Table 7. Temperature Optimization for the System Using
 [PPN][Ru(CO)₃Cl₃] as Catalyst Precursor in DMF Solvent^a

entry	<i>T</i> (°C)	time (h)	conv (%)	selec (%)	turnover
1	120	12	57	96	16
2	140	6	74	96	41
3	160	3	80	95	89
4	180	2	100	97	170
5	200	2	100	38	74

"Experimental conditions: [PPN][Ru(CO)₃Cl₃] (0.235 mmol), HCO₂CH₃ (5 mL), [formate]/[cat.] = 345, DMF (15 mL), $P(C_2H_4) = 20$ atm.

alkoxycarbonylation reaction were produced through the latter experiment at 200 °C, such a reaction did not occur. We also noted a critical influence of the temperature on the composition of the solutions recovered at the end of catalytic runs. Typically, whereas a yellow solution (IR ν (CO) 2003 (s), 1918 (vs)) was recovered when the working temperature was maintained at 160 °C or below, the red carbido complex [PPN]₂[Ru₆C-(CO)₁₆] was systematically present at the end of all catalytic runs carried out above 180 °C. Since these changes might indicate a faster deactivation of the working catalyst at high temperatures, the working temperature was maintained at 160 °C in all further experiments. To date, attempts to isolate the yellow species detectable by IR have been unsuccessful.

Influence of the Solvent. Up to 10 different solvents were examined (Table 8, and selected results in Figure 6). DMF, DMA, and NMP gave the best results, whereas *N*-methylacetamide (NMA) was found to be inefficient. Apparently, catalysis takes place only when the nitrogen atom of the amide function is disubstituted.

Relative Efficiency of [PPN][Ru(CO)₃Cl₃], [PPN]-[Ru(CO)₃Br₃], [PPN][Ru(CO)₃I₃], and RuCl₃ nH_2O + 2[Et₄N]I. The results of a comparative study of these salts under our standard experimental conditions are displayed in Table 9. It appears that (i) the order of reactivity of halide ions for the species [PPN][Ru-(CO)₃X₃] is Cl > Br > I, and (ii) the mixture RuCl₃ nH_2O



Figure 5. Temperature optimization for the catalytic system based on $[PPN][Ru(CO)_3Cl_3]$. The plots represent the evolution of the internal pressure within the reactor as a function of time for different temperatures under the experimental conditions defined in Table 7.



Figure 6. Influence of the solvent on the efficiency of the catalytic system based on $[PPN][Ru(CO)_3Cl_3]$. The plots represent the evolution of the internal pressure within the reactor as a function of time under the experimental conditions defined in Table 8.

 $+ 2[Et_4N]I$ is still only moderately active and rather unselective under the mild conditions of our experiment.

Influence of Additional Promoters. As noted above, whereas all experiments using the clusters derived from mixtures of $Ru_3(CO)_{12}$ + [PPN]Cl as catalysts precursors led to 100% conversion, the maximum conversion rate obtained with [PPN][Ru(CO)_3Cl_3] did not exceed 80%. However, it was subsequently found that addition of 1 equiv of [PPN]Cl allows us to achieve 100% conversion within 2 h (Table 10).

Triethylamine is commonly used as a cocatalyst in catalytic systems involving halide promoters. Petit and co-workers had already noted its positive influence on the activity of their system based on $RuCl_{3}nH_{2}O + 2[Et_{4}N]I$. We just noted exactly the same effect on our system, namely, a prolongation of the linear phase of

 Table 8. Influence of the Nature of the Solvent on the Activity of [PPN][Ru(CO)₃Cl₃]^a

entry	solvent	time (h)	conv (%)	selec (%)	TOF (h ⁻¹)
1	THF	5	24	59	11
2	CH ₃ CN	3	7	96	8
3	TMEDA	3	32	9	4
4	HMPA	4	75	0	0
5	DME	5	49	97	34
6	DMSO	4	46	70	32
7	DMF	3	80	95	89
8	NMP	3	77	94	85
9	DMA	3	78	95	88
10	NMA	3	0	0	0

^{*a*} Experimental conditions: [PPN][Ru(CO)₃Cl₃] (0.235 mmol), HCO₂CH₃ (5 mL), solvent (15 mL), $P(C_2H_4) = 20$ atm, T = 160 °C.

the catalysis being optimum for a ratio $[NEt_3]/[cat.] = 3$ (see Table 11).

Table 9. Effect of the Nature of the Halide on the Efficiency of $[PPN]Ru(CO)_3X_3]$; Comparison with the System Based on $RuCl_3'3H_2O + 2[Et_4N]I^a$

entry	catalyst precursor	time (h)	conv (%)	selec (%)	$TOF(h^{-1})$
1	[PPN]Ru(CO) ₃ Cl ₃]	3	80	95	89
2	[PPN][Ru(CO) ₃ Br ₃]	3	11	89	13
3	$[PPN][Ru(CO)_3I_3]$	4	2	82	2
4	$RuCl_3 \cdot 3H_2O + 2[Et_4N]I$	3	28	41	14

"Experimental conditions: catalyst precursor (0.235 mmol), HCO₂CH₃ (5 mL), DMF (15 mL), $P(C_2H_4) = 20$ atm, T = 160 °C.

Table 10. Modulation of the Activity of [PPN][Ru(CO)_3Cl_3]by Addition of [PPN]Cl^a

entry	catalyst precursor	time (h)	conv (%)	selec (%)	TOF (h ⁻¹)
1	[PPN][Ru(CO) ₃ Cl ₃]	3	80	95	89
2	[PPN][Ru(CO) ₃ Cl ₃] + [PPN]Cl	3	97	98	112

"Experimental conditions: [PPN][Ru(CO)₃Cl₃] (0.235 mmol), HCO₂CH₃ (5 mL), DMF (15 mL), $P(C_2H_4) = 20$ atm, T = 160 °C.

Table 11. Modulation of the Activity of [PPN][Ru(CO)₃Cl₃] by Addition of Variable Amounts of Thiethylamine^a

entry	[NEt3]/[cat.]	time (h)	conv (%)	selec (%)	TOF (h ⁻¹)
1	458	4	0	0	0
2	50	2	41	35	25
3	25	2	59	57	60
4	10	2	61	82	88
5	6	2	86	98	146
6	3	2	100	98	170
7	2	2	82	95	136
8	0	3	80	95	89

"Experimental conditions: [PPN][Ru(CO)₃Cl₃] (0.235 mmol), HCO₂CH₃ (5 mL), DMF (15 mL, except in run 1 where pure triethylamine was used as a solvent) $P(C_2H_4) = 20$ atm, T = 160 °C.

Table 12. Comparative Evaluation of the Salts [PPN][Ru(CO)_3I_nCl_{3-n}] (n = 0, 1, 2, 3) as Catalyst Precursors^a

entry	catalyst precursor	time (h)	conv (%)	selec (%)	$TOF(h^{-1})$
1	[PPN][Ru(CO) ₃ I ₃]	5	2	82	2
2	$[PPN][Ru(CO)_3ClI_2]$	5	84	98	58
3	[PPN][Ru(CO) ₃ Cl ₂ I]	4	100	97	86
4	[PPN][Ru(CO) ₃ Cl ₃]	2	100	98	170

" Experimental conditions: [PPN][Ru(CO)₃I_nCl_{3-n}] (n = 0, 1, 2, 3) (0.235 mmol), NEt₃ (0.705 mmol), HCO₂CH₃ (5 mL), DMF (15 mL), $P(C_2H_4) = 20$ atm, T = 160 °C.

Relative Efficiency of Mixed-Halide Complexes [PPN][Ru(CO)₃Cl_nI_{3-n}]. In order to ascertain our observation that the chloride ion is superior to the iodide, we were led to analyze the effect of a progressive substitution of the three iodide atoms of the complex [PPN][Ru(CO)₃I₃] by chloride atoms. The results shown respectively in Table 12 and Figure 7 provided further evidence that the chloride is by far the best promoter under mild experimental conditions.

The optimum performances of the catalytic system for a standard ethylene pressure of 20 atm are summarized in eq 4.

Poisonous Effect of CO. A very significant poisonous effect of CO was noted. Indeed, under the optimum experimental conditions defined in eq 4, a partial pressure of 3 atm of CO was found to inhibit almost completely the catalysis, leading to only 8% conversion and 80% selectivity. A similar poisonous effect was noted upon addition of 1 equiv of triphenylphosphine (43% conversion, 28% selectivity).

Attempted Alkoxycarbonylation Reaction. Finally, it was of interest to determine whether the



98% selectivity TOF = 170 h^{-1}

synthesis of methyl propionate could be alternately achieved via a conventional alkoxycarbonylation process starting from methanol + CO in the presence of our catalyst precursor. In a typical experiment using 0.235 mmol of [PPN][Ru(CO)₃Cl₃], 0.042 mol of methanol, 18 mL of DMF, 10 atm of C₂H₄, and 10 atm of CO, the rate of methanol conversion into methyl propionate was found to be only 69% after 6 h, thus corresponding to a turnover frequency of 27 h⁻¹, much lower than that obtained with methyl formate as a substrate.

Furthermore, an additional experiment where the reactor was loaded with nitrogen (7 atm) instead of ethylene (otherwise using the standard conditions of eq 4) revealed that the decomposition of methyl formate into MeOH + CO was limited to 7% after 2 h at 160 °C.

Evidence for the Implication of DMF in the Formation of the Active Species. When DMF solutions of the complex [PPN][Ru(CO)₃Cl₃] were heated in the absence of substrate at the temperature of the catalytic reaction, namely, 160 °C, infrared monitoring indicated the progressive formation of a new complex exhibiting two $\nu(CO)$ bands appearing at lower frequencies (2045 (s), 1975 (s) cm^{-1}) than those of the starting complex (2108 (s), 2031 (vs) cm^{-1}). The reaction was generally complete within 0.5 h, and the new compound was isolated as bright yellow crystals. An IR spectrum taken after redissolution of these crystals in dichloromethane revealed a third band at 1645 cm⁻¹ that had been previously masked in DMF solution by the characteristic ν (C=O) band of the solvent. The formulation of the complex as [PPN][Ru(CO)₂Cl₃(η^1 -OCHN(CH₃)₂)] (11), consistent with analytical results, was ascertained by an X-ray structure determination.

A perspective view of the anionic unit of [PPN][Ru-(CO)₂Cl₃(η^1 -OCHN(CH₃)₂)] (11) is displayed in Figure 8. The complex results from the replacement of a CO ligand of [PPN][Ru(CO)₃Cl₃] by a DMF molecule coordinated through the oxygen atom. However, whereas the starting compound [PPN][Ru(CO)₃Cl₃] was isolated as the *fac*-isomer (*vide supra*), the three halides of the DMF-substituted derivative adopt a *mer*-arrangement of chloride atoms. One of the two axial sites is occupied by the oxygen atom of the coordinated DMF. Though the overall geometry is indeed octahedral, the complex may be alternately regarded as an unsaturated square pyramidal fragment "Ru(CO)₂Cl₃⁻" being stabilized by a solvent molecule.

In a series of new experiments, we are now currently observing that the catalytic activity of [PPN][Ru(CO)₂Cl₃- $(\eta^1$ -OCHN(CH₃)₂)] slightly exceeds that found for [PPN][Ru(CO)₃Cl₃], due to a shortening of the initial induction period.



Figure 7. Influence of the I/Cl ratio on the efficiency of [PPN][$Ru(CO)_3I_nCl_{3-n}$] as catalyst precursor under the experimental conditions defined in Table 9.

Discussion

Polymetallic Ruthenium Carbonyl Halide Complexes: Labile Combinations of Electron Deficient Skeletons and Electron Rich Anions. The associative mechanism by which the first chloride ion is incorporated into the coordination sphere of $Ru_3(CO)_{12}$ has been well established from previous studies.¹² Let us just remind the reader here that the chloridecontaining anions corresponding to the stepwise loss of CO from the initial adduct are [PPN][Ru_3(Cl)(CO)_{11}] (1), [PPN][Ru_3(μ -Cl)(CO)_{10}] (2), and [PPN][Ru_3(μ_3 -Cl)(CO)_9] (3) (Scheme 1). The less CO rich derivative 3 is formed quantitatively in refluxing THF but is stable only in the absolute absence of CO.^{12g,h} Otherwise, it rapidly rearranges to the well known butterfly complex [PPN]-[Ru_4(μ -Cl)(CO)_{13}] (5).²⁴

The present work reveals that incorporation of a second chloride ligand can be easily achieved under thermal activation to produce a dianionic species. Such a reaction may readily take place under the conditions of many catalytic systems where $Ru_3(CO)_{12}$ is used in the presence of an excess of halide promoter. Though simple CO displacement by a chloride ligand from **3** would be expected to give a trinuclear substituted derivative of rough formula "[PPN]₂[Ru₃(Cl)₂(CO)₈]", such an intermediate is not seen, whereas the tetranuclear cluster [PPN]₂[Ru₄(μ -Cl)₂(CO)₁₁] (**4**) is isolated quantitatively in the presence of an excess of chloride (at least $\frac{1}{2}$ equiv).

For metal carbonyl complexes, aggregation via metalmetal bond formation is generally the only way to release the unsaturation created by thermally induced loss of CO. Here, capture of an additional chloride ligand may be regarded as a spare means for the cluster to protect vacant coordination sites on electron-deficient metal centers. The occurrence of a concomitant reorganization of the trimetal framework into a tetranuclear one reflects the important lability of ruthenium/carbonyl/halide aggregates. An intermolecular transfer of metal/chloride/CO fragments is obviously required in such a transformation. It may be facilitated by transient formation of halide bridges between neighboring cluster units. A relevant type of "ligand-induced aggregation" was previously observed in the dimerization of the related anionic trinuclear species [PPN][Ru₃(CN)-(CO)₁₁] to the dianionic hexanuclear species [PPN]₂[Ru₆-(μ -CN)₂(CO)₂₀], a coupling reaction assisted by the coordinated cyanide ligand.³⁵

A general observation is that the interaction of 4 with donor substrates does not give simple isolable adducts. Occupation of the apical coordination site of the unsaturated Ru center apparently triggers a complete reorganization of the polymetallic architecture. For example, addition of CO induces immediate loss of a halide ion and concomitant formation of a metal-metal bond to yield the butterfly complex 5. Even more complicated is the reaction with oxygen, which involves disruption of metal-metal bonds, intermolecular scavenging of halide ions, and encapsulation of a single oxygen atom to give [PPN]₂[Ru₄(μ ₄-O)(μ -Cl)₄(CO)₁₀] (6).

Thus, in account of the high lability of the above aggregates, it seems reasonable to ascribe their efficiency as catalyst precursors to the facile generation of active mononuclear ruthenium carbonyl halide fragments under catalytic conditions. The principal arguments consistent with such a view are the following: (i) catalysis in the presence of all the anionic ruthenium carbonyl chloride clusters considered here takes place only after an induction period (see an example in Figure 4); (ii) comparable conversion rates and selectivities are obtained, regardless of the different polymetallic architectures of these compounds, which means that there is no structure/activity relationship; (iii) all these compounds are transformed under catalytic conditions, and the principal dianionic species $[PPN]_2[Ru_6(\mu_6-C)(CO)_{16}]$ recovered at the end of the catalytic runs is only

⁽³⁵⁾ Lavigne, G.; Lugan, N.; Bonnet, J.-J. J. Chem. Soc., Chem. Commun. 1987, 957.



Figure 8. Perspective view of the anionic unit of complex 11.

moderately active and rather unselective in the production of methyl propionate.

[PPN][Ru(CO)₃Cl₃] as an Alternate Catalyst Precursor. According to Dombek,²⁷ the reaction of Ru₃- $(CO)_{12}$ with iodide salts in the presence of CO/H₂ mixtures generates the two anionic complexes [Ru₃(μ -H)(CO)₁₁]⁻ and [Ru(CO)₃I₃]⁻, acting in concert to promote syngas conversion to ethylene glycol via intermolecular hydride transfer. These complexes were also taken into account in relevant Ru-based syngas reactions in molten salts developed by Knifton and coworkers.³⁶ Furthermore, the same mixture of anionic species was used by Hidai in the alkoxycarbonylation of ethylene with MeOH + $CO.^{28}$ In that case, it was suggested that consecutive insertion of ethylene and CO into the Ru-H bond of the hydrido anion would give a propionyl intermediate, whereas a bimolecular reaction would then lead to propionyl iodide, subsequently converted into methyl propionate via reaction with methanol.28

There are significant differences between our system using methyl formate as a substrate and the one proposed by Hidai for the alkoxycarbonylation reaction using MeOH + CO. In particular, (i) we use exclusively the chloride-containing salt [PPN][Ru(CO)₃Cl₃] as a catalyst precursor, since the corresponding iodide derivative proved to be inactive under our milder reaction conditions; (ii) the addition of $[Ru_3(\mu-H)(CO)_{11}]^-$ has no detectable influence on the activity of our catalytic system; (iii) the promoter effect of Cl⁻ is observed only in the amide type solvents, whereas the former iodidepromoted alkoxycarbonylation reaction was performed in neat methanol; finally, (iv) the activity of our catalyst is quenched by small amounts of CO (3 atm), whereas a significant CO pressure is obviously required in a conventional alkoxycarbonylation process starting from methanol.

Our observation of a significant poisoning effect of CO tends to indicate that the mechanism by which methyl formate is activated *in situ* in the present case is not a simple decomposition of methyl formate to methanol and free CO followed by a conventional hydroalkoxy-carbonylation process.

One may wonder whether the catalytic system presented here and the above mentioned patented process^{11b} involve the same active species. We have presently no answer to such a question. A puzzling point is that, even though both chloride and iodide ions are claimed to be necessary in the catalytic system based on $RuCl_3 nH_2O + 2[NEt_4]I$,^{11b} we find that the chloridecontaining salt [PPN][Ru(CO)₃Cl₃] alone is active in our system and that the presence of iodide is detrimental (Figure 7). Though the turnover rates obtained with our chloride-based system do not match those reported in the patented process, it is noteworthy that (i) the respective values are not directly comparable³⁷ and (ii) those reported here were recorded under mild experimental conditions at which the former process is still only moderately active and rather unselective. Whereas the present chloride-based system appears to reach its optimum efficiency at milder conditions than recorded for other promoters, a major limiting factor is the temperature, which should not exceed 180 °C, above which the active species seems to be decomposed. This result is fully consistent with Keim's earlier observation that the halide-containing anion $[Ru_3(\mu-Cl)(CO)_{10}]^-$ is a much less efficient catalyst precursor than $Ru_3(CO)_{12}$ at 230 °C.8

Key Role of the Solvent. There is an apparent synergism in the combined effects of halide ions and amide solvents on the ruthenium-catalyzed ethylene/ formate reaction. It has been suggested that partial decomposition of DMF under catalytic conditions might play a role in the formation of the active species.¹¹ Recently, des Abbayes and co-workers reported that amines (that might be possibly obtained in small amounts via partial decomposition of DMF) catalyze the decomposition of methyl formate to methanol and CO, even in the absence of metal.³⁸ To date, the only experimental evidence we have is that DMF is involved as a ligand at the intermediate stage. We are currently attempting to determine whether it either acts as a weakly coordinated ligand stabilizing a reactive fivecoordinate intermediate or undergoes subsequent metalassisted decomposition, with possible relevance to the

⁽³⁶⁾ Knifton, J. F. In Aspects of Homogeneous Catalysis; Ugo, R., Ed.; Reidel: Dordrecht, The Netherlands, 1988; Vol. 6, p 1 (see also references therein).

⁽³⁷⁾ The best TOF value of 1450 h⁻¹ reported in the patent^{11b} was measured at 65% conversion, whereas the recently published^{11c} value of 2300 h⁻¹ was measured at 25% conversion. In the present case, an attempt to estimate the turnover frequency of our system from the linear part of the pressure plot in the best catalytic run (Figure 7) led to an approximate value of 700 h⁻¹.

⁽³⁸⁾ Ramirez Vega, F.; Clement, J.-C.; Des Abbayes, H. Tetrahedron Lett. 1993, 34, 8117.

Table 13. Crystal and Intensity Data for the Complexes $[PPN]_2[Ru_4(\mu-Cl)_2(CO)_{11}]$ (4), $[PPN]_2[Ru_4(\mu_4-O)(\mu-Cl)_4(CO)_{10}]$ (6), and $[PPN][Ru(CO)_2Cl_3(\eta^1-OCHN(CH_3)_2)]$ (11)

compd	4	6	11
formula	$C_{83}H_{60}N_2O_{11}P_4Cl_2Ru_4 (+ 1.5CH_2Cl_2)$	$C_{82}H_{60}N_2O_{11}P_4Cl_4Ru_4$	C41H37N2O3P2Cl3Ru
Fw	1860.5	1919.4	875.1
<i>a</i> , Å	18.209(2)	13.226(5)	9.000(2)
b, Å	18.877(3)	25.533(2)	21.176(2)
c, Å	13.895(2)	12.771(3)	21.080(1)
a, deg	110.70(1)	92.39(1)	90.00
β , deg	108.43(1)	114.77(3)	93.89(8)
v. deg	87.43(1)	85.92(2)	90.00
V. Å ³	4226(1)	3906(2)	4008.3(9)
Z	2	2	4
space group	triclinic $P\overline{1}$ (No. 2)	triclinic PI (No. 2)	$P2_1/c$ (No. 14)
T. °C	23	23	-140
radiation, wavelength, Å	Mo Kα, λ (Mo Kα ₁) = 0.7093 Å (r	nonochromator)	
linear abs coeff, cm ⁻¹	9.46	10.2	7.0
cryst shape	prismatic; 6 faces	prismatic; 6 faces	prismatic
boundary faces	$\{100\}, \{011\}, \{0,1,-1\}$	$\{010\}, \{011\}, \{1, -2, 0\}$	-
dist from faces to origin, cm	0.01, 0.011, 0.009	0.011, 0.018, 0.025	
min and max transm	0.812, 0.874	0.674, 0.828	0.92, 1.23
receiving aperture, mm	4.0×4.0	4.0×4.0	4.0×4.0
takeoff angle, deg	3.0	2.5	2.5
scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
scan range, deg	$0.85 \pm 0.345 \tan \theta$	$0.7 \pm 0.345 \tan \theta$	$0.8 \pm 0.345 \tan \theta$
scan speed, deg min ⁻¹	4.1	4.1	variable (4.1-16.5)
background	moving position	fixed position at both ends	moving position
θ limit, deg	1.0-23.5	1.0 - 23.0	1.0-25.0
no, of data colled	12934	11249	5512
no. of unique data used	$5493 (F_0^2 > 4\sigma(F_0^2))$	7753 $(F_0^2 > 4\sigma(F_0^2))$	$5219 (F_0^2 > 3\sigma(F_0^2))$
final no. of variables	523	460	470
$R (\text{on } F_{0})^{a}$	0.053	0.038	0.028
R_{w} (on \tilde{F}_{0})"	0.069	0.045	0.030
$w = 1/(\sigma(F_0)^2 + p^2 F_0^2)$	p = 0.03	p = 0.013 (refined value)	no weight
$S,^{h}$ Å ²	1.86	1.96	2.13

 ${}^{"}R = \sum ||F_0| - |F_c||/\sum |F_0|; R_w = [\sum w(|F_0| - |F_c|)^2/(\sum w|F_0|^2)]^{1/2}$. ^b Error in an observation of unit weight.

formation of the active species. To date, very little is known about the above mentioned yellow species which is seen by IR spectroscopy during the course of the catalysis. Attempts to isolate and characterize the latter complex are underway.

Concluding Remarks

In summary, the present contribution shows that, regardless of their nuclearity, various ruthenium carbonyl chloride complexes are susceptible to generating an active species achieving the catalytic hydroesterification of ethylene with methyl formate in amide solvents.

Due to the important lability of their ruthenium/ chloride framework, the odd aggregates investigated in the first part of this work are susceptible to producing unsaturated fragments of lower nuclearity. This is probably the clue to their efficiency as catalyst precursors.

With the mononuclear complex [PPN][Ru(CO)₃Cl₃], or its DMF-substituted derivative [PPN][Ru(CO)₂Cl₃(η^{1} - $OCHN(CH_3)_2)$], we are much closer to the active species. These complexes, which were found to be much more active than the iodide derivative $[PPN][Ru(CO)_3I_3]$, can be used in amide solvents without additives. They are of particular interest on account of their availability in high yield from commercial $RuCl_3 nH_2O$ and their ability to catalyze the hydroesterification reaction under rather mild conditions. It is hoped that, due to their simplicity, these complexes will be amenable to a detailed mechanistic study of the catalytic system. To date, there is a growing number of new catalytic processes where methyl formate is involved as a substrate and still no firm evidence for the mechanism of its metal-mediated activation.^{1,2} Though direct C-H activation has been observed in few instances, 2d,g the alternate possibility of a C-O cleavage within the ester function should be also considered as a working hypothesis, especially in light of the observation that aldehydes cannot be added to ethylene under the experimental conditions defined above.

Experimental Section

All synthetic manipulations were carried out under nitrogen atmosphere, using standard Schlenk techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl just before use. Dichloromethane was distilled over P₂O₅. Bis(triphenylphosphoranylidene)ammonium chloride, [PPN]-Cl, was obtained from Aldrich. RuCl₃*n*H₂O (*n* = 3) was purchased from Johnson Matthey. The following starting materials were prepared according to published procedures: Ru₃(CO)₁₂,³⁰ [PPN][Ru₃(Cl)(CO)₁₁] (1),^{12h} [PPN][Ru₃(μ -Cl)(CO)₁₀] (2),^{12h} [PPN][Ru₃(μ -cl)(CO)₉] (3),^{12h} [PPN][Ru₄(μ -Cl)(CO)₁₃] (5),²⁴ [PPN][Ru₃(μ - η ²-O(C₅H₄N)}(CO)₁₀],¹⁵ [PPN][Ru₃(μ - η ²-N(C₆H₅)(C₅H₄N)}(CO)₉],¹⁵ [PPN][Ru₃(μ -H)(CO)₁₁],³⁹ and [Ru(CO)₃I₂],²⁹

Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer with 0.1 mm cells equipped with CaF_2 windows. These spectra were calibrated against water vapor absorptions.

Preparation of the Complexes. Preparation of [PPN]₂-**[Ru**₄(μ -Cl)₂(CO)₁₁] (4). The complex [PPN][Ru₃(μ_3 -Cl)(CO)₉] (3) was prepared *in situ*^{12h} from Ru₃(CO)₁₂ (300 mg, 0.469 mmol) and [PPN]Cl (270 mg, 0.469 mmol) in 30 mL of freshly distilled THF. A continuous stream of argon was bubbled through the solution. Solid [PPN]Cl (135 mg, 0.235 mmol) was added, and the suspension was heated under reflux. Infrared monitoring indicated the formation of a new compound 4. The new IR bands were rapidly maximized and finally disappeared

⁽³⁹⁾ Lavigne, G.; Lugan, N.; Bonnet, J.-J. Inorg.Chem. 1987, 26, 2345.

Table 14. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors ($Å^2 \times 100$) with Esd's in Parentheses for Compound 4

atom	.x/a	<u>y</u> /b	zlc	Ueq/Uiso	atom	x/a	y/b	zlc	Ueq/Uiso
$\mathbf{R}\mathbf{u}(1)$	0.68072(7)	0.70556(6)	0.02806(9)	3.74(7)	C(46)	0.6469(5)	-0.0261(5)	0 5407(6)	5.1(4)
Ru(2)	0.76129(7)	0.84317(6)	0.1960(1)	4.32(8)	C(51)	0.6069(4)	0.0395(4)	0.8038(7)	3 1(3)
Ru(3)	0.82989(7)	0.75244(6)	0.0439(1)	4.09(7)	C(52)	0.6149(4)	-0.0201(4)	0.8429(7)	37(3)
Ru(4)	0.73626(7)	0.83847(7)	-0.0639(1)	4.82(8)	C(53)	0.5552(4)	-0.0412(4)	0.8725(7)	48(4)
C(1)	0.7060(2)	0.9288(2)	0.0894(3)	59(3)	C(54)	0.3832(1) 0.4876(4)	-0.0027(4)	0.8631(7)	5 3(4)
C(2)	0.6142(2)	0.7707(2)	-0.1046(3)	54(2)	C(55)	0.4796(4)	0.0568(4)	0.8240(7)	61(4)
C(1)	0.7585(8)	0.6553(8)	-0.065(1)	4 8(9)	C(56)	0.5393(4)	0.0780(4)	0.7944(7)	54(4)
O(1)	0.7572(6)	0.5998(6)	-0.1364(9)	6 3(8)	C(61)	0.5575(4) 0.7720(5)	0.0815(5)	0.8620(6)	39(3)
C(2)	0 5900(9)	0.6403(9)	-0.041(1)	6(1)	C(62)	0.8392(5)	0.0781(5)	0.8330(6)	5 5(4)
O(2)	0.5338(7)	0.6034(7)	-0.078(1)	9(1)	C(63)	0.0372(5)	0.0941(5)	0.9129(6)	64(5)
$\tilde{C}(3)$	0.7209(9)	0.6473(9)	0.114(1)	6(1)	C(64)	0.9175(5)	0.1135(5)	1.0217(6)	69(5)
O(3)	0.723(7)	0.6120(6)	0.114(1) 0.1673(9)	8 1(9)	C(65)	0.8504(5)	0.1159(5)	1.0507(6)	7.6(5)
C(4)	0.6509(9)	0.0120(0) 0.7868(7)	0.157(1)	4 5(9)	C(66)	0.0304(5) 0.7776(5)	0.1109(5)	0.9709(6)	5 2(4)
O(4)	0.6006(6)	0.7929(6)	0.197(9)	7 2(8)	C(71)	0.8155(6)	0.1009(3) 0.3889(4)	0.2389(8)	42(4)
C(5)	0.770(1)	0.934(1)	0.313(1)	7(1)	C(72)	0.8241(6)	0.3607(4) 0.4593(4)	0.2302(8)	64(5)
O(5)	0.7744(9)	0.994(1)	0.382(1)	11(1)	C(73)	0.8643(6)	0.4555(4)	0.1635(8)	8 4(6)
C(6)	0.7744(2)	0.7947(9)	0.302(1)	6(1)	C(74)	0.8058(6)	0.4000(4)	0.1054(8)	8 2(5)
O(6)	0.8362(8)	0.7547(5) 0.7661(8)	0.252(1)	11(1)	C(75)	0.8930(0)	0.3335(4)	0.1034(8)	8 0(5)
C(7)	0.8502(8)	0.7001(8)	0.000(1)	5(1)	C(75)	0.8672(0) 0.8470(6)	0.3333(4)	0.1140(8)	6.0(3)
O(7)	0.0000(7)	0.0000(0)	0.175(1) 0.214(1)	7 6(9)	C(81)	0.8340(6)	0.3201(4)	0.1307(3)	5.2(4)
C(8)	0.9231(7)	0.7002(0)	-0.025(1)	5(1)	C(87)	0.8076(6)	0.3730(0)	0.521(1)	0.6(6)
O(8)	0.9043(9)	0.7360(8)	-0.064(1)	10(1)	C(83)	0.8600(6)	0.3651(6)	0.521(1)	13.2(8)
C(0)	0.9323(7)	0.7309(8)	-0.00+(1)	7(1)	C(84)	0.8000(0)	0.3001(0)	0.021(1)	13.2(0)
O(0)	0.0030(9)	0.0933(8) 0.6581(7)	0.121(2) 0.167(1)	0.2(0)	C(85)	0.9587(0)	0.3646(0)	0.040(1)	11.0(9)
C(10)	0.9149(0)	0.0001(7)	-0.040(1)	9.2(9) 6(1)	C(85)	0.9031(0)	0.4000(0)	0.371(1)	7.7(5)
O(10)	0.8239(9)	0.0920(9) 0.0941(7)	-0.040(1)	11(1)	C(80)	0.7087(6)	0.3977(0)	0.471(1) 0.2557(8)	4.7(3)
C(10)	0.0010(7)	0.9241(7) 0.7746(9)	-0.189(2)	7(1)	C(91)	0.7087(0)	0.2913(3)	0.2337(8)	6 3 (4)
O(11)	0.7573(8)	0.7740(9) 0.7368(7)	-0.269(1)	11(1)	C(92)	0.0339(0)	0.2892(3) 0.2196(5)	0.137(8)	8 8(6)
P(1)	0.7373(3) 0.6778(2)	0.1985(2)	0.209(1)	3.6(2)	C(93)	0.5942(0) 0.6254(6)	0.2190(5)	0.1218(8)	0.0(0)
N(1)	0.6508(6)	0.1320(6)	0.0929(3)	3.0(2)	C(97)	0.0237(0)	0.1525(5)	0.1210(8) 0.1068(8)	9.3(0)
P(2)	0.0503(0)	0.1520(0) 0.0628(2)	0.7192(9) 0.7568(3)	3 5(2)	C(95)	0.0902(0)	0.1340(3) 0.2242(5)	0.1908(8)	7.0(0)
P(3)	0.0001(2) 0.7641(2)	0.0028(2) 0.3808(2)	0.3253(3)	4.0(2)	C(101)	0.7399(0) 0.7821(5)	0.2242(3)	0.2038(8)	38(3)
N(2)	0.7067(6)	0.5000(2) 0.4442(6)	0.3233(9)	4.0(2) 4.3(7)	C(102)	0.7021(5) 0.8087(5)	0.6329(5)	0.3107(0) 0.4780(6)	5 9(4)
P(4)	0.6942(2)	0.5216(2)	0.3440(7) 0.4257(3)	35(7)	C(102)	0.8787(5)	0.0327(5)	0.5418(6)	73(5)
$\Gamma(13)$	0.7753(6)	0.3210(2) 0.1974(5)	0.6893(6)	3.8(3)	C(103)	0.0707(5)	0.6668(5)	0.5410(0)	68(5)
C(13)	0.8348(6)	0.2448(5)	0.7773(6)	57(4)	C(105)	0.8955(5)	0.6139(5)	0.0304(0)	67(5)
C(15)	0.0040(0)	0.2396(5)	0.7768(6)	7.8(5)	C(105)	0.8255(5)	0.0100(5)	0.0712(0) 0.6075(6)	5.1(4)
C(16)	0.9784(6)	0.1869(5)	0.6884(6)	87(6)	C(100)	0.6255(5)	0.5716(5)	0.3475(6)	3.1(4)
C(17)	0.8689(6)	0.1395(5)	0.6004(6)	84(6)	C(112)	0.6138(6)	0.5710(5) 0.6445(5)	0.3968(6)	69(5)
C(18)	0.7924(6)	0.1447(5)	0.6009(6)	6.2(4)	C(112)	0.5648(6)	0.6417(5)	0.3335(6)	7.4(5)
C(21)	0.6157(5)	0.1957(5)	0.5641(7)	3.7(3)	C(114)	0.5361(6)	0.66017(5)	0.2208(6)	7 7(5)
C(22)	0.5394(5)	0.1653(5)	0.5292(7)	5.0(4)	C(115)	0.5563(6)	0.5731(5)	0.1715(6)	7.0(5)
C(23)	0.4874(5)	0.1661(5)	0.4313(7)	6.9(5)	C(116)	0.6054(6)	0.5359(5)	0.2348(6)	5.8(4)
C(24)	0.5118(5)	0.1973(5)	0.3683(7)	6.6(5)	C(121)	0.6463(5)	0.5071(4)	0.5122(8)	41(3)
C(25)	0.5882(5)	0.2277(5)	0.4032(7)	6.9(5)	C(122)	0.6447(5)	0.567(4)	0.6058(8)	7.1(5)
C(26)	0.6401(5)	0.2269(5)	0.5011(7)	5 6(4)	C(123)	0.6030(5)	0.5565(4)	0.6694(8)	8 2(5)
C(31)	0.6716(5)	0.2205(5) 0.2885(5)	0.7927(6)	3.7(3)	C(123)	0.5630(5)	0.3363(4) 0.4867(4)	0.6393(8)	7.8(5)
C(32)	0.6773(5)	0.3561(5)	0.7752(6)	4.9(4)	C(125)	0.5646(5)	0.1001(1) 0.4271(4)	0.5456(8)	7.5(5)
C(33)	0.6762(5)	0.3351(5) 0.4255(5)	0.8557(6)	7 1(5)	C(125)	0.5040(5)	0.4271(4) 0.4372(4)	0.3430(8) 0.4821(8)	5 3(4)
C(34)	0.6694(5)	0.4274(5)	0.9538(6)	7.2(5)	C(10))	0.985(3)	0.9372(4)	0.338(3)	19(3)
C(35)	0.6637(5)	0.3597(5)	0.9712(6)	6.8(5)	C(3)	0.9522(6)	0.1601(6)	0.3756(9)	23(1)
C(36)	0.6648(5)	0.2903(5)	0.8907(6)	5.8(4)	Cl(4)a	1.074(2)	0.065(2)	0.389(3)	17(2)
C(41)	0.6876(5)	-0.0200(5)	0.6472(6)	3.6(3)	Cl(4)h	1.051(2)	0.095(2)	0.295(2)	18(3)
C(42)	0.7307(5)	-0.0792(5)	0.6672(6)	4,9(4)	Cl(4)c	1.034(2)	0.065(2)	0.470(2)	20(3)
C(43)	0.7330(5)	-0.1446(5)	0.5807(6)	6.5(5)	Cl(5)	-0.018(2)	0.482(2)	-0.043(2)	18(3)
C(44)	0.6922(5)	-0.1506(5)	0.4742(6)	6.9(5)	C(201)	0.084(3)	0.475(2)	0.072(4)	25(5)
C(45)	0.6492(5)	-0.0914(5)	0.4542(6)	6.7(5)	Cl(6)	0.123(2)	0.548(2)	0.140(3)	25(4)
/				(-)			0.0 (0(2)	0(0(0)	

as the compound crystallized from the THF solution, even at reflux temperature (66 °C). After 90 min, the solution was allowed to cool and 10 mL of hexane was added. The blood red complex 4 was isolated by filtration (460 mg, 70% yield). Suitable crystals for the X-ray diffraction analysis were grown from dichloromethane/hexane mixtures. Dichloromethane molecules were subsequently found to be trapped in the lattice of these crystals (*vide infra*).

Noticeably, treatment of solutions of complex 4 with CO (1 atm, 2 min) results in the precipitation of 1 equiv of [PPN]Cl and concomitant formation of the known butterfly complex [PPN][Ru₄(μ -Cl)(CO)₁₃] (5). The reverse reaction takes place in refluxing THF within 90 min under a stream of inert gas.

4. Anal. Calcd for $C_{84}H_{62}N_2Cl_4O_{11}P_4Ru_4$ (%) (taking into account 1 mol of dichloromethane per mol of complex): C, 51.86; H, 3.21; N, 1.44. Found: C, 51.70; H, 3.09; N, 1.31. IR

 $(\nu(\rm CO),\,CH_2Cl_2):~2015~(m),\,1971~(vs),\,1960~(sh),\,1919~(m),\,1895~(vs)~1770~(s)~cm^{-1}.~~^1H~NMR~(acetone-d_6):~\delta~7.64-7.90~(m,~phenyls,~PPN^+),~5.75~(dichloromethane~solvate).$

Preparation of [PPN]₂[Ru₄(\mu_4-O)(\mu-Cl)₄(CO)₁₀] (6). The starting complex 4 was prepared as indicated above, from 300 mg of Ru₃(CO)₁₂. The crystallized product was dissolved in 30 mL of freshly distilled dichloromethane, and the solution was stirred in a beaker for 1 h at room temperature in air. The initial blood red color progressively turned yellow. After evaporation of the solvent, the solid residue was recrystallized from acetone/ethanol, providing bright yellow crystals of 6 suitable for X-ray diffraction (150 mg, 22% yield calculated from Ru₃(CO)₁₂).

6. Anal. Calcd for $C_{82}H_{60}N_2Cl_4O_{11}P_4Ru_4$ (%): C, 51.31; H, 3.16; N, 1.46. Found: C, 50.60; H, 3.04; N, 1.31. IR (ν (CO), CH₂Cl₂): 2011 (vs), 1938 (vs), 1710 (m, br) cm⁻¹.

 Table 15. Selected Interatomic Distances (Å) for 4, with Esd's in Parentheses

		Ru-R	u		
Ru(1)-Ru(3)	2.812(2)	$\mathbf{R}_{\mathbf{H}}(1) = \mathbf{R}_{\mathbf{H}}(2)$	2 870(1)	Ru(2)-Ru(3)	2.806(2)
		$R_{II}(3) - R_{II}(4)$	2.376(1)		
Ru(1)-Ru(4)	3.502(2)	114(0) 114(1)	2.100(2)	Ru(2)Ru(4)	3.463(2)
		RuC	21		
Ru(1)-Cl(1)	2.536(4)			Ru(2)-Cl(2)	2.534(4)
Ru(4)-Cl(1)	2.417(4)			Ru(4)-Cl(2)	2.416(4)
	Ru-	C (Bridging Ca	rbonyl Gr	oups)	
Ru(1) - C(1)	2.18(2)			Ru(2) - C(7)	2.13(2)
Ru(3) - C(1)	2.08(1)			Ru(3) - C(7)	2.10(1)
Ru(1) - C(4)	2.12(1)			Ru(2) - C(4)	2.14(1)
	Ru-	C (Terminal Ca	rbonyl Gr	oups)	
Ru(1) - C(2)	1.87(1)			Ru(2) - C(5)	1.87(1)
Ru(1) - C(3)	1.86(2)			Ru(2) - C(6)	1.84(2)
		Ru(3)-C(8) Ru(3)-C(9)	1.87(2) 1.81(2)		
Ru(4) - C(10)	1.82(2)		1.0 ((2)	Ru(4) - C(11)	1.84(2)
	C-0	O (Bridging Ca	rbonyl Gro	oups)	
C(1) = O(1)	1.15(2)			C(7)-O(7)	1.16(2)
		C(4) = O(4)	1.15(2)		
	C-0) (Terminal Ca	rbonyl Gro	oups)	
C(2)-O(2)	1.13(2)			C(5)-O(5)	1.14(2)
C(3)-O(3)	1.14(2)			C(6)-O(6)	1.14(2)
		C(8)-O(8)	1.15(2)		
		C(9)-O(9)	1.13(2)		
C(10)-O(10)	1.14(2)			C(11) = O(11)	1.13(2)
	Sh	ortest Intermole	cular Con	tact	
		$Ru(4) \cdot \cdot \cdot H(53)$	2.919(9)		

 Table 16.
 Selected Bond Angles (deg) for 4, with Esd's in Parentheses

	Ru-R	lu-Ru	
Ru(2) - Ru(1) - Ru(3)	59.18(4)	Ru(1) - Ru(2) - Ru(3)	59.39(4)
Ru(1) - Ru(3) - Ru(2)	61.43(4)		
Ru(1) - Ru(3) - Ru(4)	77.77(5)	Ru(2)-Ru(3)-Ru(4)	76.85(5)
	Ru-F	Ru—Cl	
Ru(2) - Ru(1) - Cl(1)	94.07(8)	Ru(1) - Ru(2) - Cl(2)	95.60(8)
Ru(3) - Ru(1) - Cl(1)	92.9(1)	Ru(3) - Ru(2) - Cl(2)	94.1(1)
Ru(3) - Ru(4) - Cl(1)	96.7(1)	Ru(3) - Ru(4) - Cl(2)	97.9(1)
	Ru-R	u-CO	
Ru(2) - Ru(1) - C(2)	148.3(5)	Ru(1) - Ru(2) - C(5)	154.3(6)
Ru(2) - Ru(1) - C(3)	92.9(4)	Ru(1) - Ru(2) - C(6)	93.3(4)
Ru(3) - Ru(1) - C(2)	152.3(5)	Ru(3) - Ru(2) - C(5)	146.0(6)
Ru(3) - Ru(1) - C(3)	92.1(5)	Ru(3) - Ru(2) - C(6)	91.3(5)
Ru(1) - Ru(3) - C(8)	147.0(4)	Ru(2) - Ru(3) - C(8)	148.6(4)
Ru(1) - Ru(3) - C(9)	96.5(6)	Ru(2) - Ru(3) - C(9)	98.1(6)
Ru(3) - Ru(4) - C(10)	88.6(6)	Ru(3)-Ru(4)-C(11)	87.0(6)
Ru(4) - Ru(3) - C(8)	94.8(5)	Ru(4) - Ru(3) - C(9)	173.7(6)
	CI-R	u-CO	
Cl(1) - Ru(4) - C(10)	91.7(6)	Cl(2) - Ru(4) - C(11)	94.5(5)
Cl(2) - Ru(4) - C(10)	173.4(6)	Cl(1) - Ru(4) - C(11)	176.1(6)
	Cl-R	lu-Cl	
Cl(1)-Ru(4)-Cl(2)	86.0(1)		

Preparation of [PPN][Ru(CO)₃Cl₃] (7) (One-Pot Procedure). The reaction was carried out in a 100 mL round bottom flask connected to a reflux condenser and equipped with a lateral gas inlet and a magnetic stir bar. $RuCl_3 nH_2O$ (1 g, 3.82 mmol) was dissolved in 20 mL of 2-ethoxyethanol. A fast stream of CO gas was bubbled through the solution which was vigorously stirred and heated under reflux. The initial brown-black color turned gold yellow over a period of 3 h. The solution was then allowed to cool down to 25 °C under CO atmosphere. At that stage, infrared monitoring in the $\nu(CO)$ region indicated the presence of three bands at 2125 (s), 2056 (s, br), and 1990 (s) cm⁻¹. The solution was maintained under CO for 7 h more, during which it became almost colorless, and finally exhibited a $\nu(CO)$ pattern characteristic of the dimer $[Ru(CO)_3Cl_2]_2$, namely, 2125 (s) and 2050 (vs) cm⁻¹. The solvent was evaporated under reduced pressure at 40-50 °C and the resulting oil was recovered with 100 mL of THF. A stoichiometric amount of [PPN]Cl (2.19 g, 3.82 mmol) was dissolved separately in the minimum amount of dichloromethane (3 mL) and added to the THF solution of the dimer. Infrared monitoring indicated an instantaneous reaction. After 5 min, the solvent was evaporated under reduced pressure and the resulting product was recrystallized in 5 mL of methanol at -25 °C. Colorless crystals of [PPN][Ru-(CO)₃Cl₃] were recovered by filtration (2.55 g, 81% yield).

7. Anal. Calcd for $C_{39}H_{30}NCl_3O_3P_2Ru$ (%): C, 56.43; H, 3.64; N, 1.69. Found: C, 55.92; H, 3.62; N, 1.88. IR (ν (CO), THF): 2108 (s), 2031 (vs) cm⁻¹.

Preparation of [PPN][Ru(CO)₃I₃] (8) from the Dimeric Species [Ru(CO)₃I₂]₂. Crystals of $[Ru(CO)_3I_2]_2^{29}$ (300 mg, 0.34 mmol) were dissolved in 20 mL of THF. Addition of a solution of [PPN]I (454 mg, 0.68 mmol) in dichloromethane (2 mL) resulted in a change in IR ν (CO) bands, indicating the formation of the anion. After evaporation of THF, the salt [PPN][Ru(CO)₃I₃] was recrystallized in the minimum amount of methanol at -25 °C and 620 mg of orange crystals were isolated (82% yield).

8. Anal. Calcd for $C_{39}H_{30}NI_3O_3P_2Ru$ (%): C, 42.41; H, 2.74; N, 1.27. Found: C, 42.35; H, 2.49; N, 1.09. IR (ν (CO), THF): 2092 (s), 2025 (vs) cm⁻¹.

Preparation of [PPN][Ru(CO)₃Cl₂I] (9). The addition of 2 mL of a dichloromethane solution containing the salt [PPN]I (508 mg, 0.76 mmol) to a portion of the ethoxyethanol solution of the dimer [Ru(CO)₃Cl₂]₂ synthesized as above (2 mL = 0.38 mmol) resulted in the immediate evolution of a lemon yellow color. After evaporation of the ethoxyethanol, the resulting oil was dissolved in the minimum amount of methanol and crystallized at -25 °C, leading to 510 mg of the salt [PPN]-[Ru(CO)₃Cl₂I] (73% yield).

9. Anal. Calcd for $C_{39}H_{30}NCl_2IO_3P_2Ru$ (%): C, 50.83; H, 3.28; N, 1.52. Found: C, 50.06; H, 3.48; N, 1.40. IR (ν (CO), THF): 2104 (s), 2028 (vs) cm⁻¹.

Preparation of [PPN][Ru(CO)₃ClI₂] (10). The complex was prepared by addition of a dichloromethane solution (2 mL) of [PPN]Cl (327 mg, 0.57 mmol) to a THF solution (20 mL) of the the dimer [Ru(CO)₃I₂]₂ (250 mg, 0.28 mmol). The color of the solution remained orange. After evaporation of the solvent, the solid residue was recovered with the minimum amount of methanol and crystallized at -25 °C, leading to 395 mg of the salt [PPN][Ru(CO)₃ClI₂] (68% yield).

10. Anal. Calcd for $C_{39}H_{30}NCII_2O_3P_2Ru$ (%): C, 46.21; H, 2.99; N, 1.38. Found: C, 46.20; H, 3.38; N, 1.16. IR (ν (CO), THF): 2096 (s), 2025 (vs) cm⁻¹.

Preparation of [PPN][Ru(CO)₂Cl₃(\eta^1-OCHN(CH₃)₂)] (11). The complex [PPN][Ru(CO)₃Cl₃] (195 mg, 0.235 mmol) was dissolved in 15 mL of dimethylformamide and heated under reflux at 160 °C. After 30 min, the initial light yellow color of the solution appeared much more intense, whereas infrared monitoring indicated spectroscopically quantitative transformation of the initial salt into a new species. After evaporation of the solvent, the resulting oil was recrystallized from acetone/heptane mixtures, leading to yellow crystals which were subsequently characterized as [PPN][Ru(CO)₂Cl₃(η^1 -OCHN-(CH₃)₂)] (118 mg, 57% yield).

11. Anal. Calcd for $C_{41}H_{37}N_2Cl_3O_3P_2Ru$ (%): C, 56.27; H, 4.26; N, 3.20. Found: C, 56.23; H, 4.20; N, 3.05. IR (ν (CO), CH₂Cl₂): 2045 (s), 1975 (s), 1645 (ms) cm⁻¹.

X-ray Structure Analyses. General Procedure. Table 13 summarizes crystal and intensity data for compounds 4, 6, and 11. Intensity data were respectively collected at 23 °C for 4 and 6, and at -140 °C for 11, on an Enraf-Nonius CAD4 diffractometer. The cell constants were obtained by least-squares refinement of the setting angles of 25 reflections in the range $26 < 2\theta(Mo \ K\alpha_1) < 30^\circ$. Data reductions for 4 and 6 were carried out using the MOLEN crystallographic

Table 17.	Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (A ²	2 \times 100) with Esd's in
	Parentheses for Compound 6	

			raie	11116365 101	Compound				
atom	x/a	y/b	z/c	$U_{\rm eq}/U_{\rm iso}$	atom	x/a	y/b	z/c	$U_{ m eq}/U_{ m iso}$
Ru(1)	0.22911(4)	0.23840(2)	-0.00729(4)	3,77(3)	C(42)	0.6924(4)	-0.0516(2)	0.2258(3)	5.0(2)
Ru(2)	0.08744(4)	0.32289(2)	0.05636(4)	3.67(3)	C(43)	0.7456(4)	-0.1015(2)	0.2353(3)	6.3(2)
Ru(3)	0.05615(4)	0.17343(2)	0.05168(4)	3.58(3)	C(44)	0.7722(4)	-0.1310(2)	0.3338(3)	6.6(2)
Ru(4)	0.17382(4)	0.24205(2)	0.26487(4)	3.59(3)	C(45)	0.7455(4)	-0.1106(2)	0.4228(3)	6.7(2)
0	0.1356(3)	0.2436(2)	0.0896(3)	3.3(2)	C(46)	0.6922(4)	-0.0606(2)	0.4133(3)	5.0(2)
Cl(1)	0.0528(1)	0.20917(7)	-0.1571(1)	4.8(1)	C(51)	0.4554(3)	0.0233(2)	0.2658(3)	3.5(2)
Cl(2)	-0.0014(1)	0.29808(7)	0.2003(1)	5.2(1)	C(52)	0.4035(3)	-0.0115(2)	0.1745(3)	5.3(2)
Cl(3)	0.2387(1)	0.13934(6)	0.0644(1)	4.7(1)	C(53)	0.2905(3)	-0.0188(2)	0.1365(3)	6.4(2)
Cl(4)	0.2505(1)	0.33195(6)	0.2420(1)	4.2(1)	C(54)	0.2295(3)	0.0086(2)	0.1898(3)	5.3(2)
C (1)	0.2979(6)	0.2356(3)	-0.1091(6)	5.1(5)	C(55)	0.2814(3)	0.0434(2)	0.2812(3)	4.8(2)
0(1)	0.3406(5)	0.2351(2)	-0.1690(5)	9.0(4)	C(56)	0.3944(3)	0.0507(2)	0.3192(3)	4.1(2)
C(2)	0.3643(6)	0.2521(3)	0.1108(6)	4.8(5)	C(61)	0.6134(3)	0.0698(2)	0.2016(4)	3.3(2)
$\tilde{O}(2)$	0.4520(4)	0.2594(2)	0.1811(4)	6.6(4)	C(62)	0.5212(3)	0.0950(2)	0.1148(4)	4.8(2)
C(3)	0.1881(5)	0.3170(3)	-0.0280(5)	3.7(4)	C(63)	0.5353(3)	0.1257(2)	0.0349(4)	6.1(2)
O(3)	0.2182(4)	0.3498(2)	-0.0694(4)	6.7(4)	C(64)	0.6415(3)	0.1312(2)	0.0418(4)	5.8(2)
C(4)	0.0589(6)	0.3947(3)	0.0377(6)	5.1(5)	C(65)	0.7337(3)	0.1060(2)	0.1286(4)	5.0(2)
O(4)	0.0388(5)	0.4387(2)	0.0227(5)	8.0(4)	C(66)	0.7196(3)	0.0753(2)	0.2085(4)	4.0(2)
C(5)	-0.0373(7)	0.3161(3)	-0.0807(7)	5.6(5)	C(71)	0.5332(3)	0.3734(2)	0.6137(4)	3.7(2)
O(5)	-0.1170(5)	0.3173(2)	-0.1643(5)	7.4(4)	C(72)	0.4779(3)	0.3346(2)	0.5341(4)	4.7(2)
C(6)	-0.0003(5)	0.0177(3)	0.0313(6)	4.7(5)	C(73)	0.5272(3)	0.3087(2)	0.4674(4)	5.9(2)
O(6)	-0.0363(4)	0.1677(3)	0.0313(0) 0.0247(4)	6 6(4)	C(74)	0.6319(3)	0.3216(2)	0.4801(4)	6.3(2)
C(7)	-0.0305(4)	0.0073(2) 0.1992(3)	0.0235(6)	4 8(5)	C(75)	0.6873(3)	0.3604(2)	0.5596(4)	6.6(2)
O(7)	-0.1778(4)	0.2110(2)	0.0233(0) 0.0044(5)	7.8(4)	C(76)	0.6379(3)	0.3863(2)	0.6264(4)	5.5(2)
C(8)	0.0971(5)	0.2110(2) 0.1733(3)	0.0044(5)	4 1(4)	C(81)	0.5302(3)	0.3672(2)	0.8356(4)	4.0(2)
O(8)	0.0971(3)	0.1733(3) 0.1422(2)	0.2239(3) 0.2813(4)	57(3)	C(82)	0.6406(3)	0.3672(2) 0.3473(2)	0.8823(4)	5.8(2)
C(0)	0.1016(6)	0.1422(2) 0.2442(3)	0.2013(4) 0.4164(6)	5.1(5)	C(83)	0.6400(3) 0.6847(3)	0.3215(2)	0.9878(4)	77(3)
O(0)	0.1910(0)	0.244(3)	0.4104(0) 0.5107(4)	8 8(4)	C(84)	0.6184(3)	0.3213(2) 0.3157(2)	1.0465(4)	8 6(3)
C(10)	0.2023(5) 0.2004(6)	0.2431(2) 0.2040(3)	0.3157(6)	45(5)	C(85)	0.0104(3)	0.3157(2) 0.3356(2)	0.9998(4)	8 5(3)
O(10)	0.3094(0)	0.2040(3)	0.3137(0)	4.3(3)	C(86)	0.4639(3)	0.3550(2)	0.9993(4)	59(2)
D(10)	0.3940(4) 0.7212(1)	0.1019(2) 0.10010(6)	0.5519(4)	3.4(1)	C(00)	0.5162(4)	0.3014(2)	0.07381(3)	3.6(2)
$\mathbf{r}(1)$	0.7525(1) 0.6462(4)	0.10010(0)	0.3137(1) 0.4227(4)	3.4(1)	C(91)	0.3102(4) 0.4042(4)	0.4000(2)	0.7331(3)	4.9(2)
$\mathbf{N}(1)$	0.0402(4)	0.0000(2)	0.4337(4)	3.7(3)	C(92)	0.4942(4) 0.5186(4)	0.5010(2)	0.0471(3)	$\frac{4}{6}$
P(2)	0.3990(1)	0.03324(0)	0.3112(1) 0.7047(1)	3.20(9)	C(93)	0.5130(4)	0.5344(2) 0.5733(2)	0.007(3)	73(2)
P(3)	0.4723(1) 0.2428(4)	0.40210(7)	0.7047(1) 0.6454(4)	3.3(1)	C(94)	0.50+9(4)	0.5755(2)	0.7033(3)	7.3(2)
D(2)	0.3428(4)	0.3974(2) 0.43040(7)	0.0434(4) 0.6047(1)	4.4(3)	C(95)	0.5809(4)	0.3390(2) 0.4860(2)	0.8518(3)	5.9(2)
P(4)	0.2283(1) 0.7744(2)	0.43049(7)	0.0047(1)	3.6(1)	C(90)	0.3023(4)	0.4669(2)	0.0516(5)	$\frac{3.9(2)}{4.2(2)}$
$C(\Pi)$	0.7744(3)	0.1400(2) 0.1708(2)	0.4420(3)	3.3(2)	C(101)	0.1933(3)	0.4000(1)	0.4700(4)	53(2)
C(12)	0.0923(3)	0.1/96(2)	0.3031(3)	4.4(2)	C(102)	0.2557(5)	0.4430(1)	0.3903(4)	60(2)
C(15)	0.7203(3)	0.2140(2) 0.2162(2)	0.3001(3)	5.4(2)	C(103)	0.2070(3)	0.7719(1)	0.2717(4)	6.6(2)
C(14)	0.8308(3)	0.2102(2) 0.1820(2)	0.3100(3)	5.1(2)	C(104)	0.1434(3) 0.1052(3)	0.5194(1)	0.2717(4) 0.3521(4)	6.0(2)
C(15)	0.9130(3)	0.1830(2)	0.3902(3)	5.7(2)	C(103)	0.1052(3)	0.3403(1)	0.3321(4) 0.4546(4)	5.5(2)
C(10)	0.8848(3)	0.1482(2)	0.4391(3)	4.0(2)	C(100)	0.1313(3) 0.2216(4)	0.3142(1) 0.4770(2)	0.4340(4) 0.7115(4)	$\frac{5.5(2)}{4.1(2)}$
C(21)	0.8571(3)	0.0665(1)	0.0147(3)	3.4(2)	C(111)	0.2210(4)	0.4770(2)	0.7113(4) 0.7223(4)	4.1(2)
C(22)	0.9237(3)	0.0904(1)	0.7190(3)	4.9(2)	C(112)	0.2003(4)	0.5257(2)	0.7223(4) 0.8033(4)	5.9(2)
C(23)	1.0198(3)	0.0636(1)	0.7905(3)	5.5(2)	C(113)	0.2366(4)	0.3020(2)	0.8032(4)	5.9(2)
C(24)	1.0494(3)	0.0128(1)	0.7697(3)	5.9(2)	C(124)	-0.0393(3)	0.3139(2)	0.3333(3)	5.9(2)
C(25)	0.9829(3)	-0.0111(1)	0.6654(3)	6.7(2)	C(125)	-0.0544(3)	0.3509(2)	0.4503(3)	0.1(2)
C(26)	0.8867(3)	0.0157(1)	0.58/9(3)	5.5(2)	C(126)	0.0269(3)	0.3862(2)	0.4699(3)	4.9(2)
C(31)	0.6729(4)	0.1377(1)	0.5988(4)	3.5(2)	C(114)	0.2068(4)	0.5508(2)	0.8732(4)	/.3(2)
C(32)	0.5941(4)	0.1160(1)	0.6265(4)	5.2(2)	C(115)	0.1621(4)	0.5021(2)	0.8024(4)	8.2(3)
C(33)	0.5483(4)	0.1449(1)	0.6931(4)	7.1(2)	C(116)	0.1696(4)	0.4652(2)	0.7810(4)	0.4(2)
C(34)	0.5813(4)	0.1954(1)	0.7320(4)	7.2(2)	C(121)	0.1232(3)	0.3845(2)	0.5727(3)	5.6(2)
C(35)	0.6601(4)	0.2170(1)	0.7043(4)	6.6(2)	C(122)	0.1381(3)	0.3475(2)	0.6559(3)	5.4(2)
C(36)	0.7059(4)	0.1882(1)	0.6377(4)	5.0(2)	C(123)	0.0568(3)	0.3122(2)	0.6363(3)	6.0(2)
C(41)	0.6656(4)	-0.0311(2)	0.3149(3)	3.4(2)	C(42)	0.6924(4)	-0.0516(2)	0.2258(3)	5.0(2)

computing package.⁴⁰ The intensities measured for these two compounds were corrected for absorption by using a numerical method based on Gaussian integration.⁴¹ Data reduction and treatment for compound 11 were carried out with the CRYS-TALS package.⁴² In that case, empirical absorption corrections were applied by using the program DIFABS.43

All three structures were solved by using the SHELXS-86 package.^{44a} The structures of 4 and 6 were refined by using the SHELX-76 package,44b whereas the structure of 11 was refined by using the CRYSTALS package.⁴² In all three cases, direct methods allowed us to locate at least the heavier atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses.

Atomic scattering factors were taken from the usual tabulations.⁴⁵ All non-hydrogen atoms of the anionic units were allowed to vibrate anisotropically. Due to the high number of variable parameters for 4 and 6, all phenyl rings of the corresponding PPN cations were treated as rigid groups with idealized geometry (C-C = 1.495 Å; C-H = 0.97 Å).

⁽⁴⁰⁾ MOLen, Package for Crystal Structure Analysis. Enraf Nonius: Delft, The Netherlands, 1990.

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^{(45) (}a) Cromer, D. T.; Waber, J. T. International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.2B. (b) Cromer, D. T.; Waber, J. T. International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.2 Vol. 4, Table 2.3.1.

 Table 18. Selected Interatomic Distances (Å) for 6, with Esd's in Parentheses

	Ru~	Ru	
Ru(1) - Ru(2)	3.063(1)	Ru(3)-Ru(4)	3.057(1)
$Ru(1) \cdot \cdot \cdot Ru(3)$	3.262(1)	$Ru(3) \cdot \cdot \cdot Ru(4)$	3.199(1)
	Ru-	·0	
Ru(1)-O	2.080(5)	Ru(3)-O	2.078(4)
Ru(2)~O	2.084(4)	Ru(4) - O	2.079(4)
	Ru-Cl (Sho	ort Bonds)	
Ru(1) - Cl(1)	2.459(2)	Ru(3)-Cl(3)	2,449(2)
Ru(2)-Cl(4)	2.463(2)	Ru(4)-Cl(2)	2.474(2)
	Ru-Cl (Lor	ng Bonds)	
$Ru(1) \rightarrow Cl(3)$	2.702(2)	Ru(3) - Cl(1)	2,836(2)
Ru(2)-Cl(2)	2.678(2)	Ru(4)-Cl(4)	2.649(2)
	Ru-C (Terminal C	arbonyl Groups)	
Ru(1)-C(1)	1.870(9)	Ru(3) - C(6)	1.850(7)
Ru(1) - C(2)	1.838(6)	Ru(3) - C(7)	1.844(8)
Ru(2) - C(4)	1.850(8)	Ru(4) - C(9)	1.848(8)
Ru(2) - C(5)	1.848(7)	Ru(4) - C(10)	1.846(7)
	Ru-C (Bridging C	arbonyl Groups)	
Ru(1) - C(3)	2.039(6)	Ru(3)-C(8)	2.033(7)
Ru(2) - C(3)	2.029(8)	Ru(4) - C(8)	2.030(6)
	C-O (Terminal C	arbonyl Groups)	
C(1) - O(1)	1.12(1)	C(6)-O(6)	1.147(9)
C(2)-O(2)	1.153(8)	C(7)-O(7)	1.15(1)
C(4) = O(4)	1.143(9)	C(9)-O(9)	1.15(1)
C(5) = O(5)	1.143(8)	C(10) = O(10)	1.140(9)
	C-O (Bridging Ca	arbonyl Groups)	
C(3)-O(3)	1.184(9)	C(8)-O(8)	1.188(9)

Specific Details for the Structure Solution of Compound 4. (a) Evidence for the Occurrence of a Square Pyramidal Geometry about the Metal Center Ru(4). After localization and refinement of the two bis(triphenylphosphine)iminium cations and of the dianionic unit $[Ru_4(\mu-Cl)_2 (CO)_{11}$]⁻, the environment of the atom Ru(4) appeared to be of square pyramidal type. The highest residual peaks in the Fourier map, all located far away from the metal center Ru-(4), were consistent with the presence of dichloromethane solvent molecules (see below the treatment of the disorder problem). Though no residual peaks appeared around the metal center Ru(4), attempts to introduce an additional CO group in an idealized position on its vacant octahedral site (in trans position relative to Ru(3)) were made with the aim of ascertaining the observed geometry. The refinement of the corresponding "phantom" C and O atoms did not converge. Furthermore, it appeared that the idealized position of the oxygen would come in unacceptable short contact with H(53). a hydrogen atom belonging to one of the two PPN cations. This drew our attention to the fact that the latter H atom was in fact "filling" the vacant octahedral site of the Ru(4) center. The intermolecular Ru $\cdot \cdot$ H contact Ru(4) $\cdot \cdot$ H(53) = 2.92 Å reflects the existence of a weak interaction, which may account for the stabilization of the unsaturated complex. The occurrence of such a short intermolecular distance also ruled out the presence of any other ligand between Ru(4) and H(53). At that stage of the refinement, the intermediate R value before introducing the solvent molecules in the model was R = 0.08.

(b) Location and Refinement of Disordered Dichloromethane Solvent Molecules in the Lattice. A total intensity loss of 9.6% was observed during data collection and corrected by using the program LINDECAY in the MOLEN package. Such a decrease might be ascribed to the loss of dichloromethane molecules from the lattice, thus rendering the determination of the exact occupancy factor of these molecules problematic. The approximate estimated value (from analysis and NMR data) was between 1 and 1.5 molecules of dichloromethane per molecule of complex 4. Solvent molecules were detected in two different "holes" in the lattice, far away from the atom Ru(4).

First Dichloromethane Molecule. The difference Fourier map provided clear evidence that the molecule was

Table 19. Selected Bond Angles (deg) for 6, with Esd's in Parentheses

	m rare	entneses	
	Ru-	0-Ru	
$\dot{Ru}(1) = O - Ru(2)$	94.7(2)	Ru(3) = O = Ru(4)	94.7(2)
Ru(1) = O = Ru(3)	103.3(2)	Ru(2) = O = Ru(4)	100.4(2)
Ru(1) = O = Ru(4)	134.6(2)	Ru(2) = O = Ru(3)	136.2(2)
	P	2	10012(2)
$R_{11}(2) - R_{11}(1) - C_{11}(1)$	Ru-1 86 60(5)	$x_u = C_1$ $P_{u}(4) = P_{u}(3) = C_1(3)$	80.10(4)
Ru(2) = Ru(1) = Cl(1) Pu(1) = Pu(2) = Cl(4)	86.09(3)	Ru(4) = Ru(3) = Cl(3) Ru(3) = Ru(4) = Cl(3)	89.19(4)
Ru(2) = Ru(2) = Cl(4) Ru(2) = Ru(1) = Cl(3)	11824(5)	Ru(3) = Ru(4) = Cl(2) Ru(4) = Ru(3) = Cl(1)	50.99(4)
Ru(1) - Ru(2) - Cl(3)	118.24(3) 118.64(4)	Ru(4) = Ru(3) = Cl(1) Ru(3) = Ru(4) = Cl(4)	115.00(4)
$\operatorname{Ku}(1)$ $\operatorname{Ku}(2)$ $\operatorname{Cl}(2)$	110.04(4)	Ru(3) = Ru(4) = Cl(4)	119.44(4)
B ₁₁ (1) C ₁₁ (1) D ₁₂ (2)	Ru-C	Cl-Ru	
Ru(1) - Cl(1) - Ru(3)	/5.68(5)	Ru(1) - Cl(3) - Ru(3)	78.41(5)
Ru(2) = CI(4) = Ru(4)	77.37(5)	$\operatorname{Ru}(2) - \operatorname{Cl}(2) - \operatorname{Ru}(4)$	76.65(6)
	Cl-F	Ru-Cl	
Cl(1) - Ru(1) - Cl(3)	80.68(5)	Cl(1) - Ru(3) - Cl(3)	78.16(6)
Cl(2) - Ru(2) - Cl(4)	80.27(6)	Cl(2) - Ru(4) - Cl(4)	80.66(6)
	Ru-R	u-CO	
Ru(2) - Ru(1) - C(1)	134.0(2)	$R_{II}(4) - R_{II}(3) - C(6)$	133.0(2)
Ru(1) - Ru(2) - C(4)	135.9(3)	Ru(3) - Ru(4) - C(9)	136.4(2)
Ru(2) - Ru(1) - C(2)	97.3(2)	Ru(4) - Ru(3) - C(7)	96 0(2)
Ru(1) - Ru(2) - C(5)	94.2(3)	Ru(3) - Ru(4) - C(10)	95.8(2)
CI-1		ninol CO Licondo)))).(())
$C(1) = \mathbb{R}_{n}(1) = C(1)$	02 5(2)	ninai CU Ligands) Cl(3) = Pu(3) = C(6)	02.0(2)
Cl(4) = Ru(2) = C(4)	92.3(2)	Cl(3) = Ru(3) = C(0)	93.9(2)
Cl(1) - Ru(1) - C(2)	173.1(2)	Cl(2) = Ru(4) = C(3) Cl(3) = Ru(3) = C(7)	92.3(2)
Cl(4) = Ru(2) = C(5)	178.4(3)	$C_{1}(2) = \mathbf{R}_{1}(4) = C_{1}(10)$	175.2(2)
C(3) - Ru(1) - C(2)	025(2)	Cl(1) = Ru(3) = C(7)	170.4(2)
Cl(2) = Ru(2) = C(5)	92.3(2)	Cl(1) = Ru(3) = C(7) Cl(4) = Ru(4) = C(10)	95.0(2)
Cl(2) = Ru(2) = C(3) Cl(2) = Ru(2) = C(4)	104 8(3)	Cl(4) = Ru(4) = C(10) Cl(4) = Ru(4) = C(0)	93.9(2)
Cl(2) = Ru(2) = C(4) Cl(3) = Ru(1) = C(2)	104.8(3)	Cl(4) = Ru(4) = C(9) Cl(1) = Ru(3) = C(6)	103.4(2)
C(3) $Ru(1)$ $C(2)$	100.9(2)	CI(1) $Ku(3)$ $C(0)$	110.0(2)
	Ru-CO (Bric	lging CO Ligands)	
Cl(1) - Ru(1) - C(3)	96.6(1)	Cl(3) - Ru(3) - C(8)	96.3(2)
Cl(4) - Ru(2) - C(3)	90.5(1)	Cl(2) - Ru(4) - C(8)	94.9(2)
Cl(3) - Ru(1) - C(3)	159.2(2)	Cl(1) - Ru(3) - C(8)	156.7(2)
Cl(2) - Ru(2) - C(3)	158.9(2)	Cl(4) - Ru(4) - C(8)	160.6(2)
	C-R	lu-C	
C(1) = Ru(1) = C(2)	88.7(3)	C(6) - Ru(3) - C(7)	85.7(3)
C(4) = Ru(2) = C(5)	86.6(3)	C(9) - Ru(4) - C(10)	87.1(3)
C(1) - Ru(1) - C(3)	93.7(3)	C(6) - Ru(3) - C(8)	92.0(3)
C(2) = Ru(1) = C(3)	90.1(2)	C(7) - Ru(3) - C(8)	90.4(3)
C(4) - Ru(2) - C(3)	94.6(3)	C(9) - Ru(4) - C(8)	95.6(3)
C(5) - Ru(2) - C(3)	91.1(3)	C(10) - Ru(4) - C(8)	88.7(3)

disordered. Indeed, the carbon atom labeled as $C(101) \ (oc$ cupancy factor = 1) was surrounded by four peaks which appeared to be chloride atoms. The highest one, subsequently labeled as Cl(3), could be correctly refined with an occupancy factor of 1.0. The three additional peaks, of lower intensity, were consistent with a statistical distribution of the second halide atom over these three sites, referred to as Cl(4a), Cl-(4b), and Cl(4c). The respective occupancy factors were determined as follows: in a first step, the refined isotropic Bvalue found for Cl(3) was ascribed to Cl(4a), Cl(4b), and Cl-(4c) and fixed. These atoms were then subsequently refined with variable occupancy factors which converged to roughly equal values (within experimental error). In a second step, the three occupancy factors were set exactly at 0.33, whereas the isotropic B's were refined. In the final stage, all five atoms of this disordered molecule were refined with anisotropic thermal parameters.

Second Dichloromethane Molecule. A second disordered molecule was located in the lattice. The lower intensities of the corresponding residual peaks indicated partial occupancy of these sites. Chart 1 provides a projection of the distribution of the corresponding electron density residues **a**, **b**, and **c**, appearing close to the inversion center noted I on the drawing (x = 0, y = 0.5, z = 0). The peaks **a***, **b***, and **c*** are respectively related to a, b, and c, through the inversion center I. The six peaks are roughly coplanar.

In account of the interatomic distances and angles between these peaks, it appeared that the three atoms of the dichloromethane molecule Cl-C-Cl could be respectively entered

 Table 20. Fractional Atomic Coordinates and Equivalent Temperature Factors (Å²) for Compound 11

			-	
atom	x/a	y/b	z/c	U(eq)
Ru(1)	0.51325(3)	0.01423(1)	0.75788(1)	0.0235
Cl(1)	0.65192(9)	0.11061(4)	0.76302(4)	0.0276
Cl(2)	0.44385(9)	0.03332(4)	0.64607(4)	0.0328
Cl(3)	0.3860(1)	0.08412(4)	0.75082(5)	0.0394
O(1)	0.5930(4)	-0.0162(4)	0.8946(1)	0.0526
O(2)	0.2435(4)	0.0833(2)	0.7899(2)	0.0638
O(3)	0.7101(2)	-0.0335(1)	0.7303(1)	0.0303
N(1)	0.9182(3)	-0.0317(1)	0.6751(1)	0.0378
C(1)	0.5642(4)	-0.0040(2)	0.8426(2)	0.0358
C(2)	0.3457(4)	0.0558(2)	0.7785(2)	0.0410
C(3)	0.7939(4)	-0.0065(2)	0.6936(2)	0.0352
C(4)	0.9614(4)	-0.0947(2)	0.6955(2)	0.044
C(5)	1.0099(5)	0.0010(2)	0.6316(2)	0.0559
P(1)	1.10208(8)	0.026638(4)	1.02159(3)	0.0194
P(2)	0.94261(8)	0.16712(4)	0,94444(3)	0.0175
N(2)	1.0596(3)	0.1987(1)	0.9943(1)	0.0215
C(10)	1.2214(3)	0.3089(2)	0.9713(1)	0.0241
C(11)	1.2428(4)	0.3738(2)	0.9771(2)	0.0365
C(12)	1.3371(4)	0.4044(2)	0.9381(2)	0.0421
C(13)	1.4095(4)	0.3709(3)	0.8935(2)	0.0436
C(14)	1,3902(4)	0.3072(2)	0.8882(2)	0.0398
C(15)	1.2959(4)	0.2754(2)	0.9269(2)	0.0322
C(20)	1.2033(3)	0.2531(2)	1.0969(1)	0.0226
C(21)	1.2919(4)	0.3002(2)	1.1252(2)	0.0336
C(22)	1.3788(4)	0.2872(2)	1.1807(2)	0.0368
C(23)	1.3782(4)	0.2281(2)	1.2067(2)	0.0364
C(24)	1.2885(4)	0.1810(2)	1.1796(2)	0.0322
C(25)	1.2002(4)	0.1936(2)	1.1245(1)	0.0264
C(30)	0.9457(3)	0.3172(1)	1.0326(1)	0.0238
C(31)	0.8809(4)	0.3506(2)	0.9810(2)	0.0306
C(32)	0.7519(4)	0.3849(2)	0.9868(2)	0.0416
C(33)	0.6862(4)	0.3854(2)	1.0438(2)	0.0435
C(34)	0.7490(4)	0.3528(2)	1.0955(2)	0.0395
C(35)	0.8795(4)	0.3190(2)	1.0905(2)	0.0323
C(40)	0.7626(3)	0.1593(1)	0.9756(1)	0.0218
C(41)	0.6412(3)	0.1377(2)	0.9368(1)	0.0270
C(42)	0.5049(4)	0.1293(2)	0.9620(2)	0.0343
C(43)	0.4885(4)	0.1431(2)	1.0252(2)	0.0354
C(44)	0.6068(4)	0.1650(2)	1.0639(2)	0.0341
C(45)	0.7445(4)	0.1729(2)	1.0393(1)	0.0275
C(50)	1.0103(3)	0.0894(1)	0.9273(1)	0.0202
C(51)	1.1270(3)	0.0628(2)	0.9655(1)	0.0245
C(52)	1.1805(4)	0.0036(2)	0.9505(2)	0.0312
C(53)	1.1181(4)	-0.0288(2)	0.8988(2)	0.0362
C(54)	0.9994(4)	-0.0036(2)	0.8627(2)	0.0351
C(55)	0.9456(4)	0.0557(2)	0.8763(1)	0.0280
C(60)	0.9152(3)	0.2070(1)	0.8693(1)	0.0191
C(61)	1.0179(3)	0.1984(2)	0.8237(1)	0.0274
C(62)	0.9995(4)	0.2298(2)	0.7663(2)	0.0343
C(63)	0.8794(4)	0.2695(2)	0.7541(2)	0.0341
C(64)	0.7781(4)	0.2786(2)	0.7993(2)	0.0328
C(65)	0.7956(3)	0.2476(1)	0.8570(2)	0.0263





on the sites $\mathbf{a}-\mathbf{b}-\mathbf{c}$. The short distance $\mathbf{a}-\mathbf{a}^* = 1.13$ Å ruled out the possibility of simultaneous occupation of the sites $\mathbf{a}-\mathbf{b}-\mathbf{c}$ and $\mathbf{a}^*-\mathbf{b}^*-\mathbf{c}^*$. A maximum occupancy factor of 0.5 could thus be expected. However, the observation of an abnormal high value for the residue **b** led us to suspect that the disorder was more intricate than expected and also involved another alternate orientation in which the atoms Cl-C-Cl would roughly correspond with the residues $\mathbf{b}-\mathbf{a}-\mathbf{b}^*$

 Table 21. Selected Interatomic Distances (Å) for 11, with Esd's in Parentheses

	Ru-Cl						
Ru(1) - Cl(1)	2.3905(8)	Ru(1)-Cl(2)	2.4309(8)				
Ru(1) - Cl(3)	2.3762(9)		. ,				
	D. 0						
$\mathbf{P}_{\mathrm{W}}(1) = \mathbf{O}(2)$	2 154(2) RU-O						
Ru(1) = O(3)	2.134(2)						
	Ru-C and	C-0					
Ru(1) - C(1)	1.855(4)	$C(1) \sim O(1)$	1.138(4)				
Ru(1) - C(2)	1.824(4)	C(2) = O(2)	1.130(4)				
	DME Lie	and					
O(3) = C(3)	1.254(4)	N(1) - C(3)	1.323(4)				
N(1) - C(4)	1.452(5)	N(1) - C(5)	1.449(5)				
	(DD) U+ C		(1) (2)				
P(1) Q(10)	[PPN] C	ation	1 500(2)				
P(1) - C(10)	1.800(3)	P(1) - C(20)	1.798(3)				
P(1) - C(30)	1.799(3)	P(1) = N(2)	1.581(3)				
P(2) - C(40)	1.796(3)	P(2) - C(50)	1.800(3)				
P(2) - C(60)	1.798(3)	P(2) - N(2)	1.584(2)				
C(10) - C(11)	1.393(5)	C(11) - C(12)	1.382(5)				
C(12) - C(13)	1.376(7)	C(13) - C(14)	1.363(7)				
C(14) - C(15)	1.390(5)	C(10) - C(15)	1.383(5)				
C(20) - C(21)	1.386(4)	C(21) - C(22)	1.390(5)				
C(22)-C(23)	1.366(6)	C(23) - C(24)	1.382(6)				
C(24) - C(25)	1.388(4)	C(20) - C(25)	1.390(4)				
C(30) - C(31)	1.393(4)	C(31) - C(32)	1.382(5)				
C(32) - C(33)	1.373(6)	C(33) - C(34)	1.379(6)				
C(34) - C(35)	1.386(5)	C(30) - C(35)	1.394(4)				
C(40) - C(41)	1.396(4)	C(41) - C(42)	1.381(4)				
C(42) - C(43)	1.382(5)	C(43) - C(44)	1.376(5)				
C(44) - C(45)	1.387(4)	C(40) - C(45)	1.393(4)				
C(50) - C(51)	1.398(4)	C(51) - C(52)	1.387(5)				
C(52)-C(53)	1.375(5)	C(53)-C(54)	1.377(5)				
C(54) - C(55)	1.383(5)	C(50) - C(55)	1.384(4)				
C(60) - C(61)	1.390(4)	C(61) - C(62)	1.380(4)				
C(62) - C(63)	1.380(5)	C(63) - C(64)	1.377(5)				
C(64) - C(65)	1.381(5)	C(60) - C(65)	1.389(4)				
			. /				

or $\mathbf{b}-\mathbf{a}^*-\mathbf{b}^*$. Thus, whereas the site **c** is only occupied by a chloride atom (labeled Cl(6) in the listing of atomic coordinates), sites a and b are each alternately occupied by C and Cl atoms. Such a disorder was treated empirically as follows: two atoms labeled as Cl(5) and C(201)) were respectively entered on the sites \mathbf{a} and \mathbf{b} with imposed B parameters of 15 $Å^2$ (average B value obtained from the first disordered molecule). The f table of carbon was used for both atoms, and the occupancy factor was set as a variable to allow the system to adjust the accurate number of electrons on each site. In the following cycles, the refined occupancy factors (Cl(5), K =1.37(3); C(201), K = 0.98(3)) were blocked, whereas the B values were refined. The occupancy factor of Cl(6) (K = 0.35-(3)) on site **c** was determined by the same procedure. In that case, the *f* table of Cl was indeed used. In the final cycles, anisotropic thermal parameters were used for all non-hydrogen atoms of the disordered molecule.

After refinement of these solvent molecules, the highest residue in the final Fourier difference map was found close to the carbons atoms C(94) and C(95) of one of the phenyl rings. The relatively high value of the final R = 0.053, is obviously due to the large number of rigid groups in the structure (12 phenyl rings in the cations).

Final atomic coordinates and $100U_{eq}$ (or $100U_{iso}$) for 4 are given in Table 14. Selected interatomic distances and interatomic bond angles of interest are given in Tables 15 and 16, respectively.

Final atomic coordinates and $100U_{eq}$ (or $100U_{iso}$) for **6** are given in Table 17. Selected interatomic distances and interatomic bond angles of interest are given in Tables 18 and 19, respectively.

Final atomic coordinates and $100U_{eq}$ (or $100U_{iso}$) for 11 are given in Table 20. Selected interatomic distances and interatomic bond angles of interest are given in Tables 21 and 22, respectively.

 Table 22. Selected Bond Angles (deg) for 11, with Esd's in Parentheses

	Ru Environment						
Cl(1) - Ru(1) - Cl(2)	90.04(3)	Cl(1) - Ru(1) - Cl(3)	177.13(3)				
Cl(1) - Ru(1) - C(1)	92.3(1)	Cl(1) - Ru(1) - C(2)	90.9(1)				
Cl(1) - Ru(1) - O(3)	88.65(6)	Cl(2)-Ru(1)-Cl(3)	89.67(3)				
Cl(2) - Ru(1) - C(1)	177.5(1)	Cl(2) - Ru(1) - C(2)	89.3(1)				
Cl(2) - Ru(1) - O(3)	88.77(6)	Cl(3) - Ru(1) - C(1)	87.9(1)				
Cl(3) - Ru(1) - C(2)	92.0(1)	Cl(3) - Ru(1) - O(3)	88.49(6)				
C(1) - Ru(1) - C(2)	91.4(2)	C(1) - Ru(1) - O(3)	90.5(1)				
C(2) = Ru(1) = O(3)	178.1(1)						
	Ru-	C-0					
Ru(1) = C(1) = O(1)	178.4(3)	Ru(1) - C(2) - O(2)	177.4(4)				
	Ru-	0-C					
Ru(1)=O(3)=C(3)	119.5(2)						
	DMF	Ligand					
O(3) - C(3) - N(1)	123.6(3)	C(3) = N(1) = C(4)	120.8(3)				
C(3) = N(1) = C(5)	121.5(3)	C(4) = N(1) = C(5)	117.6(3)				
	[PPN]	Cation					
P(1) - N(2) - P(2)	139.2(2)						
N(2) = P(1) = C(10)	112.2(1)	N(2) - P(1) - C(20)	105.9(1)				
N(2) - P(1) - C(30)	114.7(1)	N(2) - P(2) - C(40)	111.8(1)				
N(2) = P(2) = C(50)	107.5(1)	N(2) - P(2) - C(60)	115.6(1)				
C(10) - P(1) - C(20)	108.1(1)	C(10) - P(1) - C(30)	106.3(1)				
C(20) = P(1) = C(30)	109.5(1)	C(40) - P(2) - C(50)	108.4(1)				
C(40) - P(2) - C(60)	107.0(1)	C(50) - P(2) - C(60)	106.3(1)				

Tables of anisotropic thermal parameters and hydrogen coordinates for 4, 6 and 11 are available as supplementary material.

Extended Hückel MO Calculations. All calculations were carried out within the extended Hückel method,²² using the modified Wolfsberg-Helmholz formula.²³ Standard atomic parameters were taken for H, C, O, P, and Cl. The exponent (ζ) and the valence shell ionization potential $(H_{ii} \text{ in eV})$ for Ru were respectively 2.078, -8.60 for 5s and 2.043, -5.10 for 5p. The H_{ii} value for 4d was set equal to -12.20. A linear combination of two Slater-type orbitals ($\zeta_1 = 5.378, c_1 = 0.5340$; $\zeta_2 = 2.203, c_2 = 0.6365$) was used to represent the atomic 4d orbitals. The model used for the calculations was based on the idealized C_s structure of 4. The following distances (Å) were used in 4 and 4': Ru-Ru = 2.815; Ru-C(O) = 1.85; Ru-(4)-Cl = 2.42; C-O = 1.14. The $Ru-CH_3$ and $Ru-PH_3$ distances in $[RuCl_2(CO)_2(CH_3)]^{3-}$ and $[RuCl_2(CO)_2(PH_3)]^{2-}$ models were respectively set equal to 2.0 and 2.25 Å. Due to the lack of symmetry in 6, the corresponding calculations were performed on the experimental molecular structure. All the averaged idealized structures which were tested presented too large steric repulsions between ligands.

Catalytic Runs. Catalytic runs were carried out in a 100 mL stainless steel autoclave equipped with a manometer, gas and liquid inlets, and a magnetic stirrer. The general experimental procedure was as follows: the catalyst precursor was

entered as a solid into the reactor which was then rapidly closed and degased under reduced pressure. The solvent (THF or amide type solvents) and the substrate (methyl formate) were mixed together in a Schlenk tube and introduced next into the reactor. Finally, the appropriate pressure of ethylene (20 bar, representing an excess relative to the formate concentration) was supplied at room temperature. The catalytic runs were started by immersion of the reactor into a thermostated oil bath. The working temperature, measured with an internal thermocouple, was reached within 20 min. The time counter was started when the working temperature was reached. Samples were analyzed by gas chromatography on an INTERSMAT IGC 120 DFB equipped with a 1/8 in. imes 3 m column filled with 10% Carbowax 20 M on Chromosorb W 80-100 mesh. Decane was used as the internal standard. In our hands, the ruthenium-catalyzed hydroesterification of ethylene with methyl formate appeared as a clean reaction, since the only adventitious byproducts were found to be methanol, CO, and traces (always less than 2%) of diethyl ketone. Thus, standard plots were made from pure samples of methyl propionate, methanol, and diethyl ketone. In the present work, conversion rate, selectivity, turnover, and turnover frequency are respectively defined as follows:

Conversion (%) = ratio between the number of moles of methyl formate consumed, N_c , and the initial number of moles of methyl formate, N_i .

Selectivity (%) = ratio between the number of moles of methyl propionate produced, N_p , and the total number of moles of products formed throughout the reaction (methyl propionate + methanol + diethyl ketone).

Turnover number (TN) = number of moles of methyl propionate produced per mole of catalyst.

Turnover frequency (TOF) = turnover per time unit (h^{-1}) .

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Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen coordinates for the three structures (8 pages). Ordering information is given on any masthead page.

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