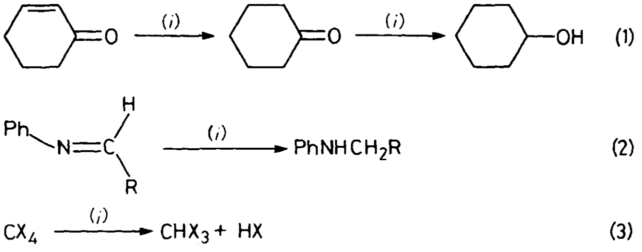
Studies on $[Ru_3(CO)_{12}]$-Catalysed Homogeneous Transfer Hydrogenation Reactions; *X*-Ray Structure of $[Ru_4(CO)_{10}Cl_2(OPh)_2]$†

Sumit Bhaduri,* Niteen Sapre, and Krishna Sharma
Alchemie Research Centre, P.O. Box 155, Thane 400 601, Maharashtra, India
Peter G. Jones
Institute Fur Anorganische und Analytische Chemie Der Technischen Universitat, Hagenring 30, 3300 Braunschweig, Federal Republic of Germany
Gene Carpenter
Department of Chemistry, Brown University, Providence, RI 02912, U.S.A.

Using $[Ru_3(CO)_{12}]$ (**1**) as the homogeneous precatalyst, transfer hydrogenations of cyclohex-2-en-1-one, benzylideneaniline, and carbon tetrahalides by donor alcohols, in particular propan-2-ol, have been studied. Conversion of cyclohex-2-en-1-one into cyclohexanol has been found to proceed *via* the intermediate formation of cyclohexanone. From the temperature dependence of the overall reaction rates, the precatalysts $[Ru_3(CO)_{12}]$ and $[Ru_4H_4(CO)_{12}]$ are involved in processes with comparable activation energies. Two catalytically active cluster complexes, $[Ru_4(CO)_{12}(C_6H_6O)]$ and $[Ru_3(CO)_{10}(C_6H_8O)]$, were isolated from the reaction of (**1**) with cyclohex-2-en-1-one. Hydrogenation of the tetranuclear cluster led to the formation of $[Ru_4H_4(CO)_{12}]$ and $[Ru_3H_2(CO)_9(C_6H_8O)]$. The reaction of complex (**1**) with benzylideneaniline gave a catalytically active cluster $[Ru_3H(CO)_9(PhNCPh)]$. With (**1**) as the precatalyst, analogues of benzylideneaniline of general formula $RC_6H_4CH{=}NPh$ can all be transfer hydrogenated, with the exception of the *o*-methoxy derivative. The complex $[Ru_3H(CO)_9(PhNCPh)]$ was found to undergo reversible carbonylation. Rational syntheses for $[Ru_3(CO)_7X_2(OR)_2]$ and $[Ru_4(CO)_{10}X_2(OR)_2]$ were designed by treating (**1**) with the appropriate alcohol and carbon tetrahalide. The *X*-ray structure of $[Ru_4(CO)_{10}Cl_2(OPh)_2]$ has been determined. The halogenoalkoxo clusters are considered to be active intermediates in the overall catalytic cycle for the transfer hydrogenations of carbon tetrahalides.

Homogeneous hydrogen-transfer reactions of a wide variety and synthetic utility are known to be efficiently catalysed by tri- and tetra-nuclear ruthenium clusters.[1] However, as for most other cluster-catalysed reactions, there is little direct evidence for the participation of cluster intermediates.[2] This is especially true for the precatalyst $[Ru_3(CO)_{12}]$ (**1**), since in most of these reactions it is converted into complexes of which few have been fully characterised. Empirical kinetic analyses to elucidate the mechanistic details of such reactions are therefore extremely difficult, if not impossible, to carry out. One way of evaluating the possible role of cluster intermediates in such complex reactions is to study the reactivities of isolated, characterised clusters.



Scheme 1. (*i*) $+Me_2CHOH$, $-Me_2CO$

The work reported here was undertaken from this standpoint. It investigates the roles of well characterised complexes isolated from the reactions of (**1**) with the reactants of three different transfer hydrogenation reactions (1)—(3). For (1) and (3), alcohols other than propan-2-ol were also used as the donor solvents. In cases where fully characterisable species could not be isolated from actual catalytic runs, conditions approximating those of the catalytic runs were used. The reactivities of the isolated species towards individual reactants of the catalytic systems were evaluated. The reaction steps, fully established in this manner, were integrated to rationalise the observed catalytic activity. Results related to the scope, efficiency, and selectivity of the three catalytic systems are also reported and commented upon. Some of these results have been communicated earlier.[3]

Results and Discussion

(*a*) *Transfer Hydrogenation of Cyclohex-2-en-1-one.*—The use of cyclic ketones or α,β-unsaturated ketones as acceptors in hydrogen-transfer systems based on complex (**1**) or $[Ru_4H_4(CO)_{12}]$ (**2**) as the catalyst has been briefly mentioned[1a]. With (**1**) or (**2**) as the precatalyst the conversion data on two model acceptors, cyclohex-2-en-1-one and cyclohexanone, under different conditions are shown in Table 1. Data obtained by using different donor alcohols show that maximum conversion is obtained when propan-2-ol is used as the solvent.

---

† 1,1,1,2,2,3,3,4,4-Decacarbonyl-2,3;3,4-di-μ-chloro-2,3,4;2,3,4-di-μ-phenoxo-tetraruthenium (*Ru*¹–*Ru*², *Ru*³–*Ru*⁴).

Supplementary data available: Further details of the structure determination (complete bond angles, H-atom co-ordinates, thermal parameters, structure factors) have been deposited at the Fachinformationszentrum Energie Physik Mathemaik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 54076

Non-S.I.-Unit employed: lbf in^{-2} = 6 895 Pa

Table 1. Transfer hydrogenation of cyclohex-2-en-1-one and cyclohexanone with different alcohols and precatalysts[a]

Catalyst	Acceptor	Donor	Conversion (%)	
			Cyclohexanone	Cyclohexanol
(1)	Cyclohexenone	Propan-2-ol in cyclohexane (1:9)[b]	7	1
(1)	Cyclohexenone	Propan-2-ol in cyclohexane (1:4)[b]	13	2
(1)	Cyclohexenone	Propan-2-ol	43	13
(1)	Cyclohexenone	Propanol	14	<1
(1)	Cyclohexenone	Benzyl alcohol	16	0
(1)	Cyclohexenone	But-2-enyl alcohol	10	2
(1)	Cyclohexanone	Propan-2-ol		60
(2)	Cyclohexenone	Propan-2-ol	45	18
(2)	Cyclohexanone	Propan-2-ol		85
(3)	Cyclohexenone	Propan-2-ol	60	40
(4)	Cyclohexenone	Propan-2-ol	45	23

[a] All reactions carried out with a catalyst:acceptor molar ratio of 1:50 in solvent (10 cm^3) at 82 °C for 6 h. For further details see Experimental section. [b] Volume ratio.

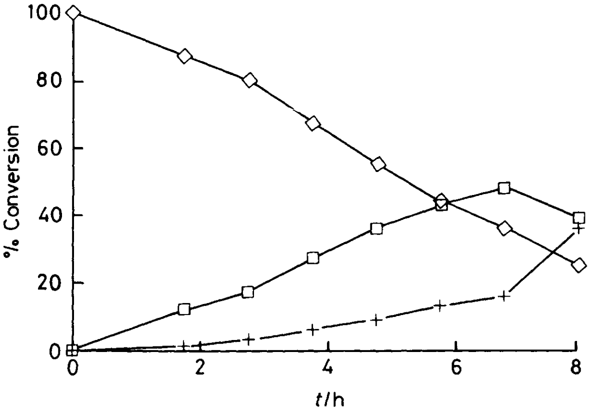


Figure 1. Time-dependent concentration profiles in $[Ru_3(CO)_{12}]$ (0.05 mmol)-catalysed conversion of cyclohex-2-en-1-one (2.5 mmol) (◇) into cyclohexanone (□) and cyclohexanol (+) by propan-2-ol (10 cm^3) at 82 °C

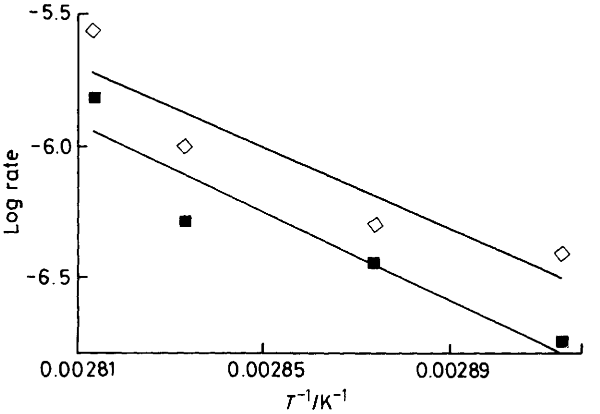
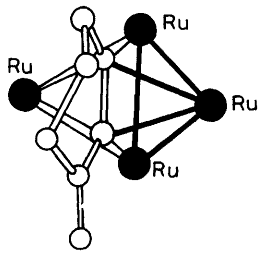
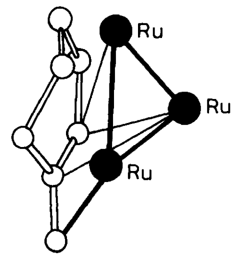


Figure 2. Plot of ln (rate) *vs.* 1/*T* for the conversion of cyclohex-2-en-1-one into cyclohexanone and cylohexanol in the presence of $[Ru_3(CO)_{12}]$ (■) and $[Ru_4H_4(CO)_{12}]$ (◇)



(3)



(4)

CO groups omitted for clarity

The time-dependent concentration profiles of cyclohex-2-en-1-one, cyclohexanone, and cyclohexanol (Figure 1) are indicative of consecutive reactions. Kinetic studies of these complex reactions have been carried out through computer-simulation techniques and will be published elsewhere. Since small quantities of complex **(2)** are formed in the reaction of **(1)** with propan-2-ol (see later) an approximate assessment of their relative efficiencies was sought. This may be obtained from the variation of rates with temperature. Considering the complexity of the system, consecutive reactions accompanied by total conversion of precatalyst into other soluble species (see later), good linearities in Arrhenius plots (Figure 2) are not expected. The exact values of the slopes are therefore of marginal significance. However, to the extent that they reflect the overall activation energies, complexes **(1)** and **(2)** appear to be of comparable activity.

As expected from earlier literature,[4] the reaction of complex **(1)** with refluxing propan-2-ol leads to the formation of small amounts (<28%) of **(2)** and acetone. No alkoxy derivatives (plausible catalytic intermediates) can be isolated under these conditions. Two cluster carbonyls, $[Ru_4(CO)_{12}(C_6H_6O)]$ **(3)** and $[Ru_3(CO)_{10}(C_6H_8O)]$ **(4)**, can however be isolated from the reaction of cyclohex-2-en-1-one with **(1)**. While **(3)**, a red-brown solid, was characterised by an *X*-ray structure determination, **(4)** a red oil, was characterised by spectroscopic techniques.[3b] It should be noted that the co-ordination modes of the organic moieties in both these complexes are not observed in osmium cluster species obtained from the reactions of $[Os_3(CO)_{12}]$ with cyclohex-2-en-1-one or cyclohexanone.[5]

The proposed mode of bonding of the C_6H_8O moiety in **(4)** is consistent with the absence of metal hydrides, ketone, and olefin functions as shown by ^1H, ^{13}C n.m.r. and i.r. data. Formation of **(3)** involves disproportionation of cyclohex-2-en-1-one; cyclohexanone has been identified as the organic product.

Both complexes **(3)** and **(4)** are active precatalysts for the transfer hydrogenation of cyclohex-2-en-1-one to cyclohexanone and cyclohexanol. The extent of conversion in both cases is somewhat higher than that obtained with **(1)** as the precatalyst (Table 1). After a significant number of turnovers (>50), i.r. spectra of the organometallic residues indicate that all the clusters **(1)**—**(4)** are converted into a common soluble carbonyl

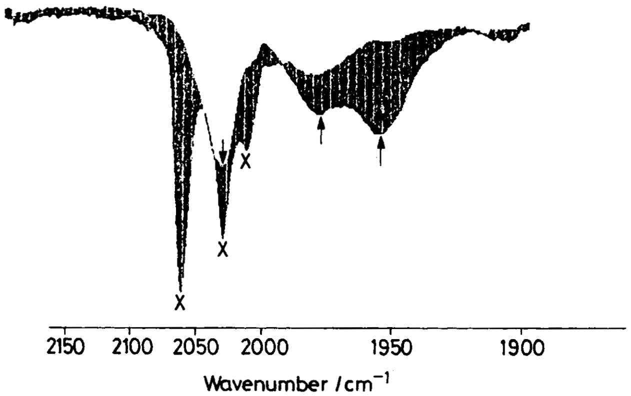
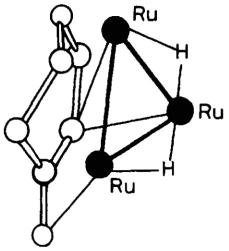
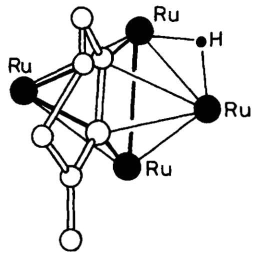


Figure 3. Infra-red spectra of a catalytic run employing $[Ru_3(CO)_{12}]$ as the catalyst at zero time and after 100 turnovers. Bands marked × are those of complex (**1**), whereas those marked ↑ or ↓ belong to the final carbonyl species also obtained when (**2**)—(**4**) are used as the precatalyst

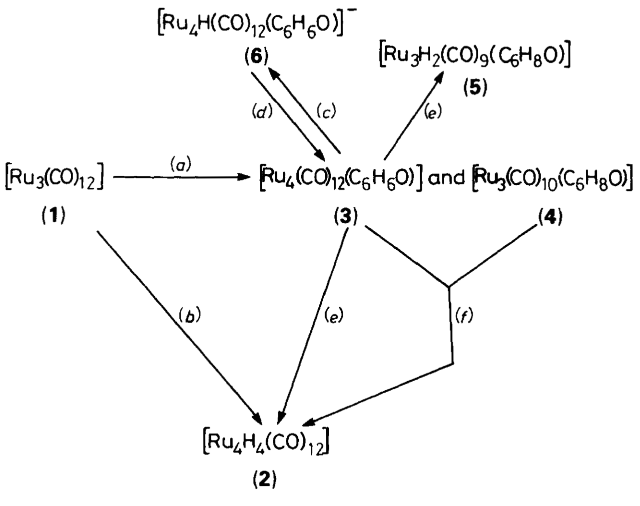


(**5**)



(**6**)

CO groups omitted for clarity. Ru—H positions arbitrary



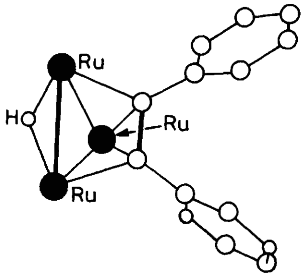
Scheme 2. (*a*) Cyclohex-2-en-1-one, 70 °C, 20 h, organic product is cyclohexanone; (*b*) propan-2-ol, 82 °C, 6 h, organic product is acetone; (*c*) BH_4^-, 27 °C, MeOH; (*d*) H^+, 27 °C; (*e*) H_2, 75 °C, 24 h, organic products are cyclohexanone and cyclohexanol; (*f*) propan-2-ol, 82 °C, 6 h, organic products are cyclohexanone and cyclohexanol

species or mixture of species (Figure 3). All attempts to purify and/or separate the individual components of this residue through chromatographic or fractional crystallisation techniques have been unsuccessful.

Table 2. Transfer hydrogenation of benzylideneaniline and analogues with $[Ru_3(CO)_{12}]$ *

Substrate	Conversion (%)
PhCH=NPh	80
o-$MeOC_6H_4CH$=NPh	0
m-$MeOC_6H_4CH$=NPh	47
p-$MeOC_6H_4CH$=NPh	45
o-MeC_6H_4CH=NPh	68
m-MeC_6H_4CH=NPh	40
p-MeC_6H_4CH=NPh	48

* All reactions carried out at 82 °C with $[Ru_3(CO)_{12}]$: substrate molar ratio of 1 : 100 in propan-2-ol (15 cm^3) for 5 h.

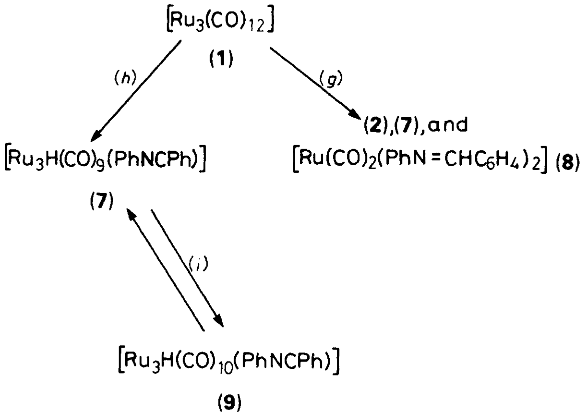


(**7**)

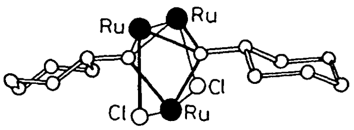
CO groups omitted for clarity

From (**3**) and (**4**) several attempts were made to synthesise cluster complexes containing a partially hydrogenated cyclohexenone moiety '$C_6H_{8+x}O$' (x = 1, 2, or 3). Both complexes when treated with propan-2-ol yield (**2**) and lose the organic ligands. In these reactions cyclohexanone and cyclohexanol are identified as co-products by gas–liquid chromatography. While hydrogenation of (**4**) yields only (**2**), hydrogenation of (**3**) leads to the formation of a mixture of (**2**) and $[Ru_3H_2(CO)_9(C_6H_8O)]$ (**5**), a species characterised on the basis of spectroscopic data. It should be noted that an analogous osmium species has been isolated from the reaction between $[Os_3(CO)_{12}]$ and cyclohexanone.[5] Thus, (**5**) may be considered as a model catalytic intermediate where transfer of the two hydrogen atoms to the co-ordinated organic ligand would lead to the formation of cyclohexanone. Reaction of complex (**3**) with $NaBH_4$ followed by treatment with $[N(PPh_3)_2]Cl$ leads to the isolation of a species formulated as $[N(PPh_3)_2][Ru_4H(CO)_{12}(C_6H_6O)]$ (**6**). The hydride attack takes place on the Ru–Ru bond rather than on the co-ordinated ligand. Treatment of (**6**) with mineral acids results in quantitative recovery of (**3**). The relationships between the clusters (**1**)—(**6**), and some of their reactions are shown in Scheme 2. While we are unable to comment upon the nature of, or the pathways that lead to, the final and common carbonyl species obtained from all the precatalysts (**1**)—(**4**), reactions (*a*), (*b*), and (*f*) are likely components of the overall catalytic cycle.

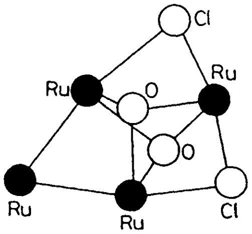
(*b*) *Transfer Hydrogenation of Benzylideneaniline.*—The conversion data for the transfer hydrogenation of benzylideneaniline and some of its analogues with complex (**1**) as precatalyst are shown in Table 2. After the catalytic reduction of benzylideneaniline (≈40 turnovers), $[Ru_3H(CO)_9(PhNCPh)]$ (**7**) and the known[6] mononuclear complex $[Ru(CO)_2(PhNCHC_6H_4)_2]$ (**8**) can be isolated from the reaction mixture through chromatographic techniques. We have earlier communicated[3a] the *X*-ray structure determination of (**7**). While (**7**) can also be obtained from the reaction of (**1**) with benzylideneaniline in refluxing hexane, (**8**) is formed only under the catalytic conditions, *i.e.* in the presence of propan-2-ol. However, unlike (**8**), which is catalytically inactive, species (**7**) is catalytically active and when used as the precatalyst can be recovered in good yield (>75%) at the end of a catalytic run (≈30 turnovers). Based on the conversion data (Table 2) for



Scheme 3. (*g*) Propan-2-ol, benzylideneaniline, cyclohexane, 80 °C, 24 h; (*h*) benzylideneaniline, cyclohexane, 80 °C, 24 h; (*i*) CO, 27 °C, 16 h



(11)



(12)

CO groups for both, and the Et groups for (**12**), are omitted for clarity

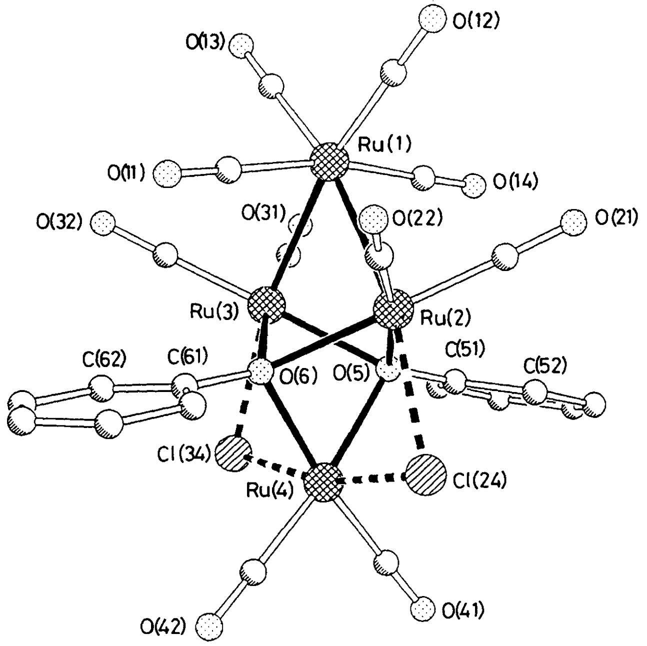


Figure 4. The structure of compound (**13**) in the crystal (radii arbitrary, H atoms omitted). The interactions Ru(2) ··· Ru(3), Ru(2) ··· Ru(4), and Ru(3) ··· Ru(4) are all > 3.1 Å and are not regarded as bonds (see text)

benzylideneaniline reduction, the catalytic activity of (**7**) is found to be approximately half that of (**1**). This suggests that apart from (**7**) some other catalytically active species are also generated from (**1**).

Species (**7**) undergoes reversible carbonylation, a reaction typical of unsaturated clusters. The apparent unsaturation of (**7**) probably lies in the fact that the hydrogen-abstracted benzylideneaniline unit 'PhNCPh' can act either as a three- or a five-electron donor, depending on the localisation or otherwise of a lone pair on the nitrogen atom. A formal electron count of 48 for both (**7**) and its carbon monoxide adduct [$Ru_3H(CO)_{10}$(PhNCPh)] (**9**) is achieved if the 'PhNCPh' moiety is assumed to act as a five- and a three-electron donor in (**7**) and (**9**) respectively. In view of the fact that carbonylation proceeds under ambient conditions, an alternative explanation involving reversible breaking of one Ru–Ru bond and a formal electron count of 50 in (**9**) seems less likely. Attempts to isolate (**9**) as a solid result in decarbonylation and formation of (**7**). It is probable that the catalytic activity of (**7**) is associated with the facile reversible formation of its unsaturated form. Support for such a view comes from the fact that no conversion is achieved with *o*-$MeOC_6H_4CH$=NPh as the substrate, and that [$Ru_3H(CO)_9$(*o*-$MeOC_6H_4C$=NPh)] undergoes *irreversible* carbonylation to give an isolable carbon monoxide adduct. However, no n.m.r., u.v.–visible, or i.r. spectroscopic evidence could be found for adduct formation between (**7**) and either benzylideneaniline or propan-2-ol. Reactions of complexes (**1**) and (**7**)—(**9**) are summarised in Scheme 3.

It is apparent that structures analogous to that of (**7**) and derived from *o*-RC_6H_4CH=NPh would entail steric interactions, the magnitude of which would depend on the nature of the 'R' group. The remarkable difference in the conversions of the *ortho*-substituted methyl and methoxy derivatives of benzylideneaniline, and the stabilities of the corresponding carbonyl adducts of the analogues of (**7**), may partly be due to differences in these steric interactions.

(*c*) *Transfer Hydrogenation of* CX_4 (X = Cl *or* Br).—Activation of chloroalkanes by complex (**1**) has been studied in detail by Eady *et al.*[7] Blum and Shvo[1a] have briefly referred to the ability of CCl_4 to act as an acceptor in hydrogen-transfer reactions. We have confirmed that (**1**) can act as an efficient (> 100 turnovers in 4 h at 82 °C) precatalyst in the reaction of CX_4 and propan-2-ol to give CHX_3 and acetone. Use of other alcohols such as cyclohexanol or ethanol results in somewhat lower (< 50 turnovers) conversions than those obtained with propan-2-ol. Under similar conditions catalytic reduction of CHX_3 to CH_2X_2 could not be achieved.

The organometallic residues obtained at the end of the catalytic runs (> 50 turnovers) were found to contain small amounts (< 10%) of [$\{Ru(CO)_3X\}_2$] (**10**), a species known[8] to be formed in the reaction between (**1**) and CHX_3. Since no other fully characterisable organometallic complex could be isolated from the catalytic reaction mixture, the reactions of (**1**) with donor alcohols and CX_4 were studied with relative concentrations of reactants different from those used in the catalytic runs. By maintaining higher (**1**):CX_4 and (**1**):alcohol ratios than in the catalytic runs, two alkoxo clusters [$Ru_3(CO)_7X_2(OR)_2$] and [$Ru_4(CO)_{10}X_2(OR)_2$] (X = Cl or Br, R = cyclohexyl or ethyl) could be isolated. The *X*-ray structural characterisations of (**11**) and (**12**) have been recently reported.[3c,9]

The relative amounts of tri- and tetra-nuclear alkoxo clusters depend on the particular halogen and alcohol employed. It is interesting that the reaction of CX_4, (**1**), and propan-2-ol, the most active donor, led to (**2**) rather than any alkoxo cluster; the alkoxo intermediates probably undergo facile β-hydride elimination. The generality of the above-mentioned synthetic procedure was verified further by using phenol as the alcohol. In this case only the tetranuclear species [$Ru_4(CO)_{10}X_2(OPh)_2$] is obtained with both CCl_4 and CBr_4. The tetranuclear chloro derivative (**13**) was characterised by single-crystal *X*-ray diffraction studies (Figure 4).

The atomic co-ordinates and bond parameters of complex (**13**) are listed in Tables 3 and 4. The long Ru(2) ··· Ru(3),

Table 3. Atomic co-ordinates (× 10^4) for complex (**13**)

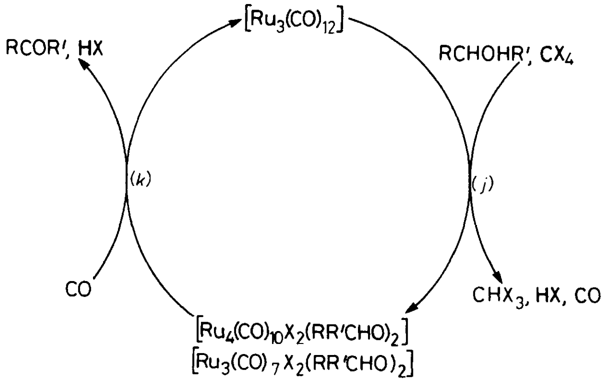
Atom	*x*	*y*	*z*
Ru(1)	3 279.2(2)	3 151.6(2)	917.2(1)
Ru(2)	2 989.3(2)	3 805.1(2)	2 501.1(1)
Ru(3)	4 333.2(2)	1 371.6(2)	2 041.5(1)
Ru(4)	4 050.8(2)	1 875.6(2)	3 899.5(1)
C(11)	1 281(3)	1 819(3)	777(2)
C(12)	2 461(3)	4 627(3)	364(2)
C(13)	3 707(3)	2 305(3)	−59(2)
C(14)	5 307(3)	4 401(3)	1 293(2)
C(21)	3 679(3)	5 710(3)	2 355(2)
C(22)	1 124(3)	4 042(3)	2 029(2)
C(31)	5 951(3)	1 589(3)	1 568(2)
C(32)	3 422(3)	−139(3)	1 236(2)
C(41)	5 565(3)	2 401(3)	4 895(2)
C(42)	2 856(3)	655(3)	4 497(2)
C(51)	6 524(2)	4 095(3)	3 371(1)
C(52)	6 699(3)	5 454(3)	3 717(2)
C(53)	8 121(3)	6 337(3)	4 053(2)
C(54)	9 356(3)	5 851(3)	4 056(2)
C(55)	9 177(3)	4 511(4)	3 728(2)
C(56)	7 754(3)	3 605(3)	3 383(2)
C(61)	1 158(2)	465(2)	2 601(1)
C(62)	994(3)	−965(3)	2 366(2)
C(63)	−380(3)	−1 961(3)	2 293(2)
C(64)	−1 562(3)	−1 547(3)	2 457(2)
C(65)	−1 379(3)	−142(3)	2 720(2)
C(66)	−16(3)	874(3)	2 789(2)
O(11)	119(3)	1 062(3)	690(2)
O(12)	2 000(3)	5 487(3)	59(2)
O(13)	3 988(3)	1 820(3)	−610(1)
O(14)	6 483(3)	5 129(2)	1 497(1)
O(21)	4 094(3)	6 890(2)	2 247(2)
O(22)	−2(2)	4 243(3)	1 741(2)
O(31)	6 926(2)	1 716(3)	1 260(1)
O(32)	2 866(3)	−1 069(2)	726(1)
O(41)	6 489(2)	2 728(2)	5 492(1)
O(42)	2 097(2)	−71(2)	4 833(2)
O(5)	5 074(2)	3 182(2)	3 030(1)
O(6)	2 536(2)	1 479(2)	2 673(1)
Cl(24)	3 022.2(6)	3 811.8(6)	4 066.1(4)
Cl(34)	5 023.6(6)	100.3(6)	3 386.7(4)

Table 4. Bond lengths (Å) in complex (**13**)

Ru(1)–Ru(2)	2.745(1)	Ru(1)–Ru(3)	2.748(1)
Ru(1)–C(11)	1.957(3)	Ru(1)–C(12)	1.944(3)
Ru(1)–C(13)	1.950(3)	Ru(1)–C(14)	1.939(2)
Ru(2)–C(21)	1.830(2)	Ru(2)–C(22)	1.839(3)
Ru(2)–O(5)	2.213(2)	Ru(2)–O(6)	2.218(1)
Ru(2)–Cl(24)	2.552(2)	Ru(3)–C(31)	1.840(3)
Ru(3)–C(32)	1.832(2)	Ru(3)–O(5)	2.213(1)
Ru(3)–O(6)	2.210(2)	Ru(3)–Cl(34)	2.581(2)
Ru(4)–C(41)	1.868(2)	Ru(4)–C(42)	1.870(3)
Ru(4)–O(5)	2.153(2)	Ru(4)–O(6)	2.144(1)
Ru(4)–Cl(24)	2.367(2)	Ru(4)–Cl(34)	2.374(2)
C(11)–O(11)	1.130(3)	C(12)–O(12)	1.115(4)
C(13)–O(13)	1.123(4)	C(14)–O(14)	1.124(3)
C(21)–O(21)	1.139(3)	C(22)–O(22)	1.134(3)
C(31)–O(31)	1.133(4)	C(32)–O(32)	1.142(3)
C(41)–O(41)	1.128(3)	C(42)–O(42)	1.118(3)
C(51)–C(52)	1.374(4)	C(51)–C(56)	1.367(4)
C(51)–O(5)	1.407(2)	C(52)–C(53)	1.376(3)
C(53)–C(54)	1.372(5)	C(54)–C(55)	1.347(5)
C(55)–C(56)	1.387(3)	C(61)–C(62)	1.389(4)
C(61)–C(66)	1.371(4)	C(61)–O(6)	1.394(2)
C(62)–C(63)	1.383(4)	C(63)–C(64)	1.364(5)
C(64)–C(65)	1.373(5)	C(65)–C(66)	1.386(3)

Ru(2) ··· Ru(4), and Ru(3) ··· Ru(4) separations are not regarded as bonds; Ru(4) is thus not involved in metal–metal interaction. The average of the Ru(2)–Ru(4) and Ru(3)–Ru(4) separations, 3.145 Å, is similar to the corresponding chloride-bridged distances, 3.159 and 3.122 Å, in (**11**) and (**12**) respectively.[3c,9a] In all the clusters (**11**)—(**13**) the Ru–Cl distances show marked asymmetry, the bonds to Ru(2) and Ru(3) in (**13**) being *ca.* 0.2 Å longer than those to Ru(4). The presence of two two-centre two-electron metal–metal bonds in (**13**) can be rationalised in terms of a formal electron count of 68 (PhO being regarded as a 5e donor and bridging Cl as a 3e donor).

The clusters (**11**) and (**12**) were tested as precatalysts and found to be active for the reduction of CX_4 to CHX_3 by the corresponding alcohols. Species (**10**) however possessed marginal catalytic activity. During the course of the catalytic runs the clusters (**11**) and (**12**) are converted into some other soluble carbonyl species (i.r. evidence). As in the case of (**1**) as the precatalyst, only small (< 10%) quantities of (**10**) are recovered from the organometallic residues in all three cases. The carbonylation of (**11**) and (**12**) under the conditions approximating those employed for catalysis (alkanol, 82 °C, $P_{co} \approx 500$ lbf in^{-2}), has been found to give (**1**) in good and low (< 10%) yields respectively. Thus, as shown in Scheme 4, a hypothetical catalytic cycle involving (**11**), (**12**), and analogous isopropoxo clusters as reactive catalytic intermediates may be proposed. However, it is certainly possible that (**11**) and (**12**) are spectator species rather than actual catalytic intermediates. The organic products CHX_3 and RCOR′ in steps (*j*) and (*k*) have been identified by g.l.c. and n.m.r. spectroscopy. Under these conditions a small amount of (**2**) is also formed, probably from reaction of (**1**) with the alkanol. However, we are unable to comment upon the deactivation pathways and this is an obvious shortcoming of Scheme 4 as a model catalytic cycle.



Scheme 4. R = R′ = Me; R = Me, R′ = H; $\overset{\frown}{R\ R'}$ = C_5H_{10}; X = Cl or Br

Experimental

General Techniques and Materials.—All reactions and manipulations were carried out under an atmosphere of dry nitrogen unless specified otherwise. Benzylideneaniline, its analogues, and the clusters (**1**) and (**2**) were synthesised by literature procedures.[10–12] Cyclohex-2-en-1-one and substituted benzaldehydes were purchased from Aldrich and used without further purification unless specified otherwise. Propan-2-ol was purified by refluxing over CaO and subsequent distillation. Infra-red and n.m.r. spectra were recorded on a PE 781 and a Brucker 80-MHz instrument, the ^{13}C n.m.r. spectrum of (**4**) and the ^1H n.m.r. spectrum of (**3**) and (**6**) on a Brucker 500-MHz instrument. Mass spectra were recorded on a A.E.I. MS 12 instrument at Universita Di Milano by Dr. E. Cessarotti.

Temperature-programmed gas chromatographic analyses were performed on a Shimadzu GC 9A instrument.

Crystal Structure Determination of [$Ru_4(CO)_{10}Cl_2(OPh)_2$].—*Crystal data.* $C_{22}H_{10}Cl_2O_{12}Ru_4$, $M_r = 941.5$, triclinic, space group $P\bar{1}$, $a = 9.498(2)$, $b = 9.687(2)$, $c = 16.355(3)$ Å, $\alpha = 91.23(2)$, $\beta = 103.24(2)$, $\gamma = 105.15(2)°$, $U = 1\,408.5$ Å^3, $Z = 2$, $D_c = 2.22$ g cm^{-3}, $F(000) = 896$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu = 2.3$ mm^{-1}, orange prism, 0.7 × 0.4 × 0.25 mm.

Data collection and reduction. 8 414 Profile-fitted intensities were recorded on a Stoe-Siemens four-circle diffractometer (monochromated Mo-K_α radiation, $2\theta_{max.}$ 60°). An absorption correction based on ψ scans was applied, with transmission factors 0.77—0.93. Averaging equivalents gave 8 207 unique reflections ($R_{int} = 0.015$), of which 7 359 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX, modified by its author G. M. Sheldrick). Cell constants were refined from 2θ values of 50 reflections in the range 20—23°.

Structure solution and refinement. The Ru atoms were located by inspection of the Patterson function; further atoms were identified in successive difference syntheses after appropriate refinement. The structure was subjected to anisotropic full-matrix least-squares refinement on *F*. Isotropic H atoms were included using a riding model. The final *R* value was 0.025, with R' 0.025. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.000\,05F^2$. An extinction correction of the form $F_{corr} = F/[1 + xF^2/\sin 2\theta]^{0.25}$ was applied, where x refined to $3.2(1) \times 10^{-6}$. 362 Parameters; *S* 1.9; maximum Δ/σ 0.09; maximum electron density 0.5 e Å^{-3} near Ru(1).

Final atomic co-ordinates are presented in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and bond angles.

Catalytic Experiments.—These experiments were carried out in a double-jacketed two-necked vessel with a flat bottom, maintained at a constant temperature by a flow of water through the outer jacket. Cyclohex-2-en-1-one and benzylideneaniline reductions were carried out at 82 °C with complex (**1**) (32 mg, 0.05 mmol) and substrate (2.5 or 5 mmol) in propan-2-ol (10 or 15 cm^3) over various reaction times. Homogeneity of the catalytic systems was established by light scattering and retention of catalytic activity in Celite-filtered solutions. Samples were withdrawn at suitable time intervals and subjected to g.c. analyses. Experiments with other cluster precatalysts, other donor alcohols, and analogues of benzylideneaniline were carried out in a similar fashion.

The reductions of CX_4 were also carried out by the same general procedure. Experiments where CHX_3 was identified by n.m.r. spectroscopy were carried out in a reduced volume (2 cm^3) of propan-2-ol. The reactions requiring high pressures of CO were carried out in a Parr pressure reactor.

Syntheses of complexes (**3**) *and* (**4**). Cyclohex-2-en-1-one (96 mg, 1 mmol) was added to a suspension of [$Ru_3(CO)_{12}$] (100 mg, 0.156 mmol) in hexane (25 cm^3) and the mixture refluxed for 20 h. The resulting dark red-brown solution was filtered and the filtrate was analysed by g.c. to establish the presence of cyclohexanone. It was then subjected to column chromatography. Elution with hexane yielded unreacted [$Ru_3(CO)_{12}$] (10 mg, 0.016 mmol). Subsequent elution with hexane–dichloromethane (1:1) gave complexes (**4**) (15 mg, 0.022 mmol) and (**3**) (40 mg, 0.048 mmol) respectively. I.r. (in hexane): (**3**), 2 098w, 2 071s, 2 048vs, 2 024s, 1 943m, and 1 680w; (**4**) 2 104vw, 2 093w, 2 076m, 2 056vs, 2 032w (sh), 2 020s, 2 004s, 1 990w, and 1 890m cm^{-1}. N.m.r.: ^1H in CD_2Cl_2, (**3**) δ 3.38 (2 H, t), 2.70 (2 H, t), and 2.18 (2 H, q); (**4**), 2.19 (2 H, m), 1.59 (4 H, m), and 1.26 (2 H, m); no Ru–H signals for (**3**) or (**4**) between δ 0 and −60; $^{13}C-\{^1H\}$ (in $CDCl_3$), (**4**), δ 51.37, 37.98, 29.65 (2C), 24.32, and 19.90 p.p.m. Molecular ion peaks: (**3**), 834 with 12 successive CO losses; (**4**), 679 with 10 successive CO losses (Found: C, 25.8; H, 0.90. Calc. for $C_{18}H_6O_{13}Ru_4$: C, 25.9; H, 0.70. Found: C, 28.3; H, 1.3. Calc. for $C_{16}H_8O_{11}Ru_3$: C, 28.3; H, 1.2%).

Hydrogenation of complex (**3**). Complex (**3**) (40 mg, 0.048 mmol) in cyclohexane (10 cm^3) was heated under an atmosphere of hydrogen at 75 °C for 24 h. Gas chromatography of the resulting yellow solution showed the presence of cyclohexanone and cyclohexanol. It was then subjected to column chromatography with hexane–dichloromethane (10:1) as the eluant. Complexes (**2**) (16 mg) and (**5**) (12 mg) were obtained. I.r. of (**5**) (in hexane): 2 112s, 2 082vs, 2 064vs, 2 042vs, 2 019vs, 1 997s, 1 965w (sh), and 1 675w (in KBr), ν(C=O) at 1 500 cm^{-1}. ^1H N.m.r. (in $CDCl_3$): δ 2.30 (2 H), 1.3 (6 H), −16.2, and −20.4. Molecular ion peak: 653 with nine successive CO losses (Found: C, 27.8; H, 1.5. Calc. from $C_{15}H_{10}O_{10}Ru_3$: C, 27.6; H, 1.5%).

Reaction of complex (**4**) with hydrogen, carried out in a similar fashion, led to quantitative formation of (**2**) and cyclohexanone and cyclohexanol as the organic products.

Reaction of complex (**3**) *with* $NaBH_4$: *synthesis of* (**6**). To a solution of complex (**3**) (50 mg, 0.06 mmol) in dry methanol (5 cm^3) was added $NaBH_4$ (11 mg, 0.3 mmol). The reaction mixture was stirred for 5 min and colour changed to dark red-brown. After addition of [$N(PPh_3)_2$]Cl (172 mg, 0.3 mmol), the solution was cooled at 0 °C for 72 h to give red-purple microcrystals of [$N(PPh_3)_2$][$Ru_4H(CO)_{12}(C_6H_6O)$] (17 mg, 0.012 mmol). I.r. (in tetrahydrofuran, thf): 2 060s, 2 032vs, 1 996vs, 1 982vs, 1 972s (sh), 1 958s, and 1 930m cm^{-1}. ^1H N.m.r. (sodium salt in CD_3OD): δ 2.90 (3 H, t), 2.28 (2 H, t), 1.82 (2 H, q), and at −19.03 (Ru–H) (Found: C, 47.6; H, 2.8; N, 1.00: Calc. for: $C_{54}H_{37}NO_{13}P_2Ru_4$: C, 47.2; H, 2.7; N, 1.00%).

Treatment of complex (**6**) *with* $HClO_4$. The salt [$N(PPh_3)_2$][$Ru_4H(CO)_{12}(C_6H_6O)$] (15 mg, 0.01 mmol) in acetone (2 cm^3) and $HClO_4$ (1 mg, 0.01 mmol) was stirred for 5 min. The solution was taken to dryness, extracted with hexane, and cooled to give complex (**3**) (8 mg, 0.009 mmol).

Synthesis of complex (**7**). Benzylideneaniline (27 mg, 0.15 mmol) and complex (**1**) (64 mg, 0.1 mmol) in cyclohexane (30 cm^3) were refluxed for 24 h. The resulting red-brown solution was subjected to column chromatography with hexane as the eluant. A small amount of (**2**) (7 mg, 0.009 mmol) was followed by (**7**) (33 mg, 0.045 mmol). Subsequent elution with hexane and dichloromethane gave another yellow fraction. The spectral data for this fraction did not match those of (**8**), and it was found to be inactive as a precatalyst. Characterisation of this species was not pursued. I.r. of complex (**7**) (in hexane): 2 094s, 2 070s, 2 038vs, 2 028s, 2 008s, 2 000s (sh), and 1 984s cm^{-1}. ^1H N.m.r. [in $(CD_3)_2CO$]: δ 7.3 (m) and −18.1 (Ru–H) (Found: C, 36.2; H, 1.6; N, 1.9. Calc. for $C_{22}H_{11}NO_9Ru_3$; C, 35.9; H, 1.5; N, 1.9%).

Synthesis of Complex (**8**). Benzylideneaniline (27 mg, 0.15 mmol), complex (**1**) (64 mg, 0.1 mmol), and propan-2-ol (2 cm^3) in cyclohexane (28 cm^3) were refluxed for 24 h. The resultant brown solution, when subjected to column chromatography with hexane as an eluant, gave complexes (**2**) (6 mg, 0.008 mmol) and (**7**) (30 mg, 0.041 mmol). Subsequent elution with hexane and dichloromethane gave another yellow fraction, which on the basis of spectroscopic data was identified as complex (**8**) (13 mg, 0.025 mmol).

Carbonylation of complex (**7**). A solution of complex (**7**) (7 mg, 0.01 mmol) in hexane (10 cm^3) was stirred under an atmosphere of CO for 16 h. Monitoring by i.r. spectroscopy showed quantitative conversion of (**7**) into (**9**). On passing nitrogen through the solution, (**9**) was converted back into (**7**). Removal of solvent under a stream of CO also led to the conversion of (**9**) into (**7**). I.r. of (**9**) (in hexane): 2 098m, 2 080w, 2 064vs, 2 048s, 2 026vs, 2 010s, 2 004s (sh), and 1 990m cm^{-1}. ^1H N.m.r. [in $(CD_3)_2CO$]: δ 7.2 (m) and −14.6.

Carbonylation of [$Ru_3H(CO)_9$(*o*-$MeOC_6H_4C$=NPh)] was carried out in a similar fashion to give the carbonyl adduct, which was isolated by solvent evaporation and crystallised from n-hexane. I.r. of [$Ru_3H(CO)_9$(*o*-$MeOC_6H_4C$=NPh)] (in hexane): 2 089s, 2 065vs, 2 032vs, 2 020vs, 2 004s, 1 995w (sh), 1 980m, and 1 971s cm^{-1}. ^{1}H N.m.r. [in $(CD_3)_2CO$]: δ 7.2 (m, 9 H), 3.7 (s, 3 H), and −18.3 (Ru–H) (Found: C, 35.8; H, 1.6; N, 1.6. Calc. for $C_{23}H_{13}NO_{10}Ru_3$: C, 36.0; H, 1.7; N, 1.8%). I.r. for [$Ru_3H(CO)_{10}$(*o*-$MeOC_6H_4C$=NPh)]: 2 100m, 2 062vs, 2 048s, 2 026s, 2 006s, 1 990w, and 1 790m cm^{-1}. ^{1}H N.m.r. [in $(CD_3)_2CO$]. δ 7.2 (m, 9 H), 3.75 (s, 3 H), and −14.4 (Ru–H) (Found: C, 36.0; H, 1.6; N, 1.7. Calc. for $C_{24}H_{13}NO_{11}Ru_3$: C, 36.3; H, 1.6; N, 1.8%).

Syntheses of complexes (**11**)—(**13**). Cyclohexanol (38 mg, 0.38 mmol), complex (**1**) (24 mg, 0.038 mmol), and CCl_4 (5 mg, 0.032 mmol) in cyclohexane (25 cm^3) were refluxed for 19 h. The resultant red-brown solution, when subjected to thin-layer chromatography with n-hexane as eluant, yielded a mixture of (**1**) and (**2**) (combined yield 10 mg), (**11**) (6 mg, 0.01 mmol), and trace quantities of [$Ru_4(CO)_{10}Cl_2(OC_6H_{11})_2$]. Reaction of complex (**1**) with ethanol and CCl_4 to give mainly (**12**) and trace quantities of [$Ru_3(CO)_7Cl_2(OEt)_2$] was carried out in a similar fashion. Complex (**12**) was identified by comparison with literature spectroscopic data.[9] The reactions of (**1**) with CBr_4 and cyclohexanol or ethanol were carried out in a similar manner. Synthesis of (**13**) was also carried out by the same general procedure.

I.r. of (**11**) (in cyclohexane): 2 076w, 2 060s, 2 036s, 2 008s, 1 992vs, and 1 780m cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): δ 3.05 (1 H), 2.17 (4 H), and 1.53 (6 H); no Ru–H signal between δ +10 and −60 (Found: C, 29.55; H, 2.80. Calc. for $C_{19}H_{22}Cl_2O_9Ru_3$: C, 29.70; H, 2.85%). I.r. of (**13**) (in hexane): 2 108m, 2 083s, 2 036vs, 2 006w, and 1 963s cm^{-1}. ^{1}H N.m.r. [in $(CD_3)_2CO$]: δ 8.13 (1 H, d), 7.64 (2 H, t), and 7.35 (1 H, t); no Ru–H signal between δ 0 and −40 (Found: C, 28.10; H, 1.15. Calc. for $C_{22}H_{10}Cl_2O_{12}Ru_4$: C, 28.05; H, 1.05%).

Reaction of complexes (**3**) *and* (**4**) *with propan-*2*-ol.* Complex (**3**) (16 mg, 0.02 mmol) was heated in propan-2-ol (5 cm^3) at 80 °C for 6 h. G.l.c. analysis of the solution established the presence of cyclohexanone and cyclohexanol. Thin-layer chromatography of the resultant solution yielded complex (**2**) (3 mg, 0.004 mmol). Reaction of (**4**) with propan-2-ol was carried out in a similar fashion with the same results.

Carbonylation of complexes (**11**) *and* (**12**). Complex (**11**) (8 mg, 0.01 mmol) in cyclohexanol (3 cm^3) was heated at 82 °C under a CO pressure of 500 lbf in^{-2} for 4 h. After venting the gas, the presence of cyclohexanone was established by g.c. analysis. The formation of complex (**1**) and trace quantities of (**2**) was inferred on the basis of solution i.r. spectra and finally (**11**) (4 mg, 0.006 mmol) was isolated by t.l.c. The carbonylation of complex (**12**) was carried out in a similar fashion.

Acknowledgements

The authors thank IEL Limited and the Fonds der Chemischen Industrie for support of this work. *X*-Ray intensity measurements were carried out at the Inorganic Chemistry Institute, University of Göttingen, West Germany.

References

1 (*a*) Y. Blum and Y. Shvo, *J. Organomet. Chem.*, 1984, **263**, 93 and refs. therein; (*b*) A. Basu, S. Bhaduri, and K. Sharma, *ibid.*, 1987, **319**, 407; (*c*) M. Bianchi, U. Maffeoli, P. Frediani, G. Menchi, and F. Piacenti, *ibid.*, 1982, **240**, 59; **236**, 375; (*d*) M. Bianchi, U. Maffeoli, G. Menchi, P. Frediani, S. Pratesi, F. Piaceuti, and G. Botteghi, *ibid.*, 1980, **198**, 73.

2 R. Whyman, in 'Transition Metal Clusters,' ed. B. F. G. Johnson, Wiley, New York, 1980; L. Marko and A. Vizi-Orosz, in 'Metal Clusters in Catalysis,' eds. B. C. Gates, L. Guczzi, and H. Knozinger, Elsevier, Amsterdam, 1986.

3 (*a*) A. Basu, S. Bhaduri, K. Sharma, and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1987, 1126; (*b*) *J. Organomet. Chem.*, 1987, **328**, C34; (*c*) S. Bhaduri, N. Y. Sapre, K. R. Sharma, and P. G. Jones, *J. Organomet. Chem.*, 1989, **364**, C8.

4 C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 838.

5 K. A. Azam, A. J. Deeming, and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 1981, 91.

6 R. L. Bennett, M. I. Bruce, B. L. Goodall, M. Iqbal, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1972, 1787.

7 C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1976, 1706.

8 A. Mantovani and S. Cenini, *Inorg. Synth.*, 1976, **16**, 51.

9 (*a*) B. F. G. Johnson, J. Lewis, J. M. Mace, P. R. Raithby, and M. D. Vargas, *J. Organomet. Chem.*, 1987, **321**, 409; (*b*) C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 477.

10 A. I. Vogel, 'Textbook of Practical Organic Chemistry,' 4th edn., Longman Group Ltd., 1978, p. 672.

11 C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, and M. C. Malatesta, *J. Chem. Soc., Dalton Trans.*, 1980, 383.

12 S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942.

Received 20*th June* 1989; *Paper* 9/02598G