clusters like [$Zn_4(C_5H_5)_4Ni_2(C_5Me_5)_2$] and, less probably, [$Zn_2(C_5Me_5)_2Zn_2(C_5H_5)_2Ni_2(C_5Me_5)_2$] should have been formed and the formation of $Zn_4Ni_2(C_5H_5)_6$ could not be accounted for.

The rate-determining step in the cluster formation reaction is the nickel insertion in step 2. This is deduced from the following facts. First, although a reaction already takes place at room temperature, cluster formation is only observed after a period of heating and therefore step 1 is not rate-determining. Second, the reaction that involved heating of the reaction mixture after a 24-h room-temperature reaction period results in the exclusive formation of the mixed product $Zn_4Ni_2(C_5H_5)_4(C_5Me_5)_2$. This indicates that the rate-determining step is prior to step 3, which is the displacement of a second COD molecule by an organozinc species. If the rate-determining step would follow step 3, this displacement could also be accomplished, instead of by $Zn(C_5Me_5)_2$, by some—still unreacted—more reactive $Zn(C_5H_5)_2$. This would, however, lead to the formation of the symmetric $Zn_4Ni_2(C_5H_5)_6$ cluster. This particular postulate was confirmed by the result from the reaction carried out *without* initial room-temperature stirring. In this case the rates of the various steps become comparable, and then $Zn(C_5H_5)_2$ can indeed compete with $Zn(C_5Me_5)_2$ in step 3 and formation of $Zn_4Ni_2(C_5H_5)_2$ does also occur. The high yield of $Zn_4Ni_2(C_5H_5)_4(C_5Me_5)_2$ in the reaction with initial stirring at room temperature also points to the exclusion of step 3 as rate determining. If this was not the case, a lower yield or the mixed-metal, mixed-ligand cluster, when compared to the reaction of $Zn(C_5H_5)_2$ and $Ni(COD)_2$, would be expected from a step in which the bulky $Zn(C_5Me_5)_2$ species must react.

The high yield with which the new cluster can be isolated can be ascribed to the stabilizing influence of the C_5Me_5 ligand on the $Zn_2Ni(C_5H_5)_2(C_5Me_5)$ radical formed in step 5. Compared to reactions involving other cyclopentadienyl systems, this permethyl ligand appears to decrease the amount of decomposition of this type of trimetallic species.

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Supplementary Material Available: Listings of hydrogen atom positions, thermal parameters, bond distances, and bond angles involving hydrogen atoms (7 pages); a listing of the F_o and F_c values (12 pages). Ordering information is given on any current masthead page.

Reaction of Triphenylphosphine with the Anionic Cluster $[HRu_3(CO)_{11}]^-$ Revisited: Isolation, Crystal Structure, and Isomerization of $[NEt_4][HRu_3(CO)_8(PPh_3)(PPhC_6H_4)]$

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The reaction of the cluster anion $[HRu_3(CO)_{11}]^-$ with PPh_3 in refluxing THF results in the formation of the orthometalation product $[HRu_3(CO)_8(PPh_3)(PPhC_6H_4)]^-$ (**3**). The cluster anions $[HRu_3(CO)_{10}(PPh_3)]^-$ (**1**) and $[Ru_3(CO)_9(PPh_3)]^{2-}$ (**2**) are supposed to be intermediates in this reaction. The protonation of **3** yields the neutral cluster $H_2Ru_3(CO)_8(PPh_3)(PPhC_6H_4)$ (**4**); however, the deprotonation of **4** with potassium selectride gives anion **5**, an isomer of **3**, differing in the position of the hydride bridge. The structure of **3** was determined by a single-crystal X-ray analysis of the tetraethylammonium salt. Crystals are monoclinic, space group $P2_1$, with the unit-cell parameters $a = 13.250$ (4) Å, $b = 14.467$ (4) Å, $c = 12.667$ (8) Å, $\beta = 99.97$ (2)°, and $Z = 2$. The structure was solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to $R = 0.0576$ and $R_w = 0.0697$ for 1339 observed reflections [$I \geq 2\sigma(I)$]. The longest edge of the triangular cluster is bridged by the hydride. The orthometalated phosphinidene ligand interacts with the three metal atoms: the phosphorus bridges two ruthenium atoms, while the third Ru atom is bonded to a carbon atom of the phosphinidene ligand.

Introduction

The reaction of the cluster anion $[HRu_3(CO)_{11}]^-$ with triphenylphosphine has been investigated in a detailed kinetic study by Ford et al.[2,3] The kinetic data suggest the reversible formation of the monosubstitution product $[HRu_3(CO)_{10}(PPh_3)]^-$ (**1**). Although this anion was not

$$[HRu_3(CO)_{11}]^- + PPh_3 \rightleftharpoons \underset{\mathbf{1}}{[HRu_3(CO)_{10}(PPh_3)]^-} + CO$$

isolated, evidence for the existence of **1** in solution was provided by a ^1H NMR signal at δ −11.91 ppm displaying

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(2) Taube, D. J.; van Eldik, R.; Ford, P. C. *Organometallics* **1987**, *6*, 125–129.

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Table I. Spectroscopic Data of Complexes 1–5

complex	IR ν(CO),[a] cm^{-1}	^1H NMR,[c] ppm	^{31}P NMR,[c] ppm	^{13}C NMR,[e] ppm
1	2052 m, 2045 w, 1999 s, 1975 s, 1963 m, 1940 sh, 1712 br	7.45 (m, 15), −11.87 (d, 1; 5.4 Hz)	33.9	204.8 (m), 285.5 (d, 62.1 Hz)
2	2035 s, 2019 s, 1990 sh, 1965 vs (br), 1770 br, 1615 br	7.43 (m, 30), 3.57 (q, 16), 1.28 (t, t, 24)	31.5 (d, 7.6 Hz), 32.4 (d, 7.6 Hz)	205.3 (m), 282.1 (d, 29.9 Hz), 303.7 (t, 29.9, 29.9 Hz)
3	2039 s, 1993 vs, 1972 s, 1929 m, 1906 sh	7.33 (m, 24), 3.15 (q, 8), 1.19 (t, t, 12), −15.30 (d, d, 1; 14.5, 15.3 Hz)	40.0 (d, 12.9 Hz), 132.5 (d, 12.9 Hz)	
4	2072 m, 2065 vw, 2048 s, 2040 vs, 2006 s, 1992 m, 1980 w[b]	7.47 (m, 24), −14.01 (d, d, d, 1; 2.8, 9.5, 17.4 Hz), −17.22 (d, t, 1; 2.8, 10.0 Hz)[d]	27.4 (d, 160.0 Hz), 130.2 (d, 160.0 Hz)	
5	2035 sh, 2020 m, 1994 s, 1967 vs, 1946 m, 1921 m	7.44 (m, 24), 3.15 (q, 8), 1.18 (t, t, 12), −17.76 (d, d, 1; 9.4, 29.9 Hz)	43.3 (d, 4.2 Hz), 239.8 (d, 4.2 Hz)	

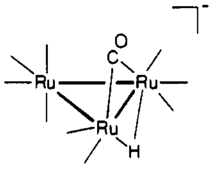
[a] In the CH_3CN. [b] In n-pentane. [c] In CD_3CN, 30 °C. [d] In $CDCl_3$, 30 °C. [e] In CD_2Cl_2, −95 °C.

a ^{31}P–^1H coupling of 5.4 Hz.[3,4] Further support comes from the infrared data of the reaction solution containing a mixture of $[HRu_3(CO)_{11}]^-$ and another anionic species assumed to be 1.[3,4] The fact that attempts to isolate 1 in a pure form had failed prompted us to reinvestigate the reaction of the anionic cluster $[HRu_3(CO)_{11}]^-$ with triphenylphosphine in THF solution, in particular, since the catalytic properties of 1 would be interesting in comparison with those of $[HRu_3(CO)_{11}]^-$.[5-8] In this paper we report the synthesis, the structure, and the isomerization of the cluster anion $[HRu_3(CO)_8(PPh_3)(PPhC_6H_4)]^-$ (3), isolated in the form of the tetraethylammonium salt as the final product from the reaction of $[HRu_3(CO)_{11}]^-$ with PPh_3 in THF solution.

Results and Discussion

The reaction sequence of $Na[HRu_3(CO)_{11}]$ with triphenylphosphine in THF solution is best monitored by ^1H NMR spectroscopy (Figure 1). Only after a few minutes the ^1H resonance assigned to the hydride bridge of 1[3,4] appears; it is observed together with the hydride signal of the starting complex $[HRu_3(CO)_{11}]^-$. The spectra clearly reveal that decomposition of 1 already takes place before the conversion of $[HRu_3(CO)_{11}]^-$ into 1 is completed. Within 2 h both hydride signals disappear without a new resonance in the hydride region of the ^1H NMR spectrum being detected. Obviously, the intermediate, the anionic species 2, does not contain a hydride ligand. However, when the reaction solution is refluxed, the hydride signal of the final product, the cluster anion 3, shows up. Contrary to 1 and 2 the cluster anion 3 can be easily isolated as the tetraethylammonium salt from methanol.

Both the sodium or the tetraethylammonium salt of 1,



1

obtained by evaporation of the solvent after a 15-min reaction time, are always contaminated with the starting complex $[HRu_3(CO)_{11}]^-$. The spectroscopic data that can be obtained from these mixtures, however, fully support the interpretation of the kinetic data given by Ford et al.[2,3] The constitution of 1 can be unequivocally deduced from the ^1H, ^{31}P, and ^{13}C NMR and IR spectra (Table I); the ^1H NMR resonance upfield δ −10 ppm shows the hydride ligand to be in a μ_2-bridging position; the ^{31}P–^1H coupling constant of 5.4 Hz is indicative of the phosphorus ligand occupying an equatorial position at one of two bridgehead ruthenium atoms. Accordingly, a single ^{31}P resonance is observed with a chemical shift typical for a PPh_3 ligand. Both the ν(CO) IR absorptions and the ^{13}C NMR spectrum [doublet at δ 285.5 ppm ($J(^{31}P$–$^{13}C)$ = 62.1 Hz)] indicate the existence of the μ_2-carbonyl ligand at the same edge as the μ_2-hydride bridge.

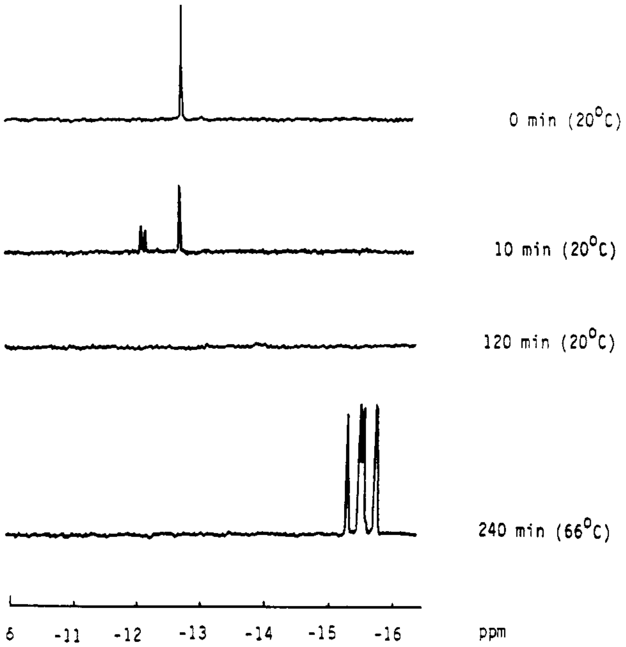
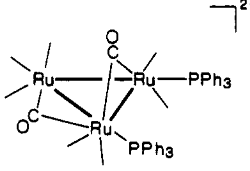


Figure 1. ^1H NMR spectra (hydride region) of a THF-d_8 solution containing $[NEt_4][HRu_3(CO)_{11}]$ and PPh_3 (1:1).

The cluster anion 2 emerging from the decomposition of 1 shows no hydride resonance in the ^1H NMR spectrum.



2

The infrared spectrum exhibits six bands in the ν(CO) region, two of them can be attributed to bridging carbonyl ligands on the basis of the low wavenumbers (Table I).

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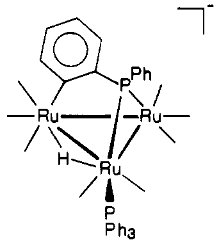
Two ^{13}C signals are observed in the region of the bridging carbonyls, one being coupled to one and the other being coupled to two phosphorus atoms [δ 282.1 ($J(^{31}P-^{13}C)$ = 30.0 Hz), 303.7 ($J(^{31}P-^{13}C)$ = 30.0, 30.0 Hz)]. The ^{31}P NMR spectrum indicates with two signals the presence of two nonequivalent PPh$_3$ ligands. On the basis of these data, we assume **2** to represent a dianionic trinuclear cluster containing two carbonyl bridges and two PPh$_3$ ligands without any plane or center of symmetry. However, with the assumption of a complete H/D exchange with the deuterated solvent, a disubstituted monoanion, [HRu$_3$(CO)(PPh$_3$)$_2$]$^-$, cannot be excluded for species **2**.

The anionic cluster **3** gives rise to a hydride signal in the ^{1}H NMR spectrum, which appears as doublet of doublets due to coupling with two different phosphorus atoms (Table I). Accordingly, two ^{31}P NMR signals are observed with a ^{31}P–^{31}P homospin coupling constant of 12.9 Hz; the resonance at δ 40.0 ppm is assigned to the terminal PPh$_3$ ligand, whereas the signal at δ 130.2 ppm arises from the bridging phosphinidene ligand. The infrared spectrum of **3** exhibits five ν(CO) absorptions in the typical region of terminal carbonyl ligands. The spectroscopic data are in accordance with the results of a single-crystal X-ray structure determination of the [NEt$_4$]$^+$ salt of **3** (see below).



3

The structural characterization of **3** also supports the existence of **1** and **2** being intermediates in the reaction of [HRu$_3$(CO)$_{11}$]$^-$ with PPh$_3$ to yield **3**. The substitution of a carbonyl ligand in [HRu$_3$(CO)$_{11}$]$^-$ by PPh$_3$ to give **1** seems to be followed by the substitution of a second carbonyl and the deprotonation of the cluster to give **2**. The conversion of **1** into **2** takes place even at 0 °C avoiding an excess of PPh$_3$. In the final step one of the phenyl substituents of one of the two PPh$_3$ ligands is orthometalated with liberation of benzene to give **3**. The deprotonation–protonation sequence in these transformations is not well understood; presumably PPh$_3$ can act as a proton acceptor. A debatable point in this sequence remains the precise nature of **2**, the characterization of which lacks ambiguity due to impurities always present in the isolated tetraethylammonium salt of **2**. The structure of **3** has been determined by an X-ray diffraction analysis using a single crystal of the tetraethylammonium salt. The structure of the cluster anion [HRu$_3$(CO)$_8$(PPh$_3$)(PPhC$_6$H$_4$)]$^-$ (**3**) is shown in Figure 2 including the atom-numbering scheme; selected bond distances and angles for **3** are given in Table II. The Ru atoms form a scalene triangular cluster with the longest edge, Ru(1)–Ru(3) = 3.008 (4) Å, bridged by the hydride ligand. The hydride H(1), clearly found in the difference Fourier map, is practically coplanar with the metal triangle, the dihedral angle between the Ru triangle and the hydride bridge being 1.1°. The Ru(1)–H(1) and Ru(3)–H(1) distances, 1.87 and 1.80 Å, and the Ru(1)–H(1)–Ru(3) angle, 110°, are as expected for this kind of bridge. The presence of the unique hydride bridge on the Ru(1)–Ru(3) edge is also confirmed by the metal distance, as the hydride bridge on a metal cluster normally causes the lengthening of the bridged metal bond, and by the wide C(7)–Ru(3)–Ru(1) and Ru(3)–Ru(1)–P(2) angles, 118 (1) and 114.3 (3)°, respectively, indicating that the equatorial carbonyl and phosphorus are bent away from the bridged edge.

Scheme I. The Reaction of Na[HRu$_3$(CO)$_{11}$] with PPh$_3$ in THF Solution.

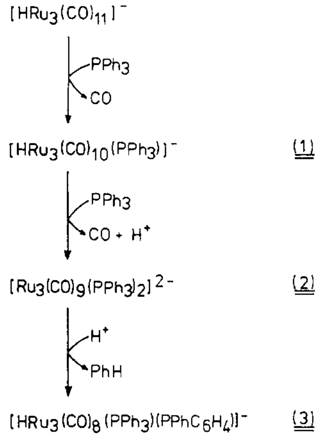


Table II. Selected Bond Distances (Å) and Angles (deg) in the Anion of 3

Ru(1)–Ru(2)	2.813 (5)	Ru(3)–C(7)	1.82 (3)
Ru(1)–Ru(3)	3.008 (4)	Ru(3)–C(8)	1.84 (5)
Ru(2)–Ru(3)	2.899 (4)	Ru(3)–C(10)	2.13 (4)
Ru(1)–P(1)	2.355 (10)	C(1)–O(1)	1.18 (3)
Ru(2)–P(1)	2.305 (11)	C(2)–O(2)	1.21 (4)
Ru(1)–P(2)	2.328 (11)	C(3)–O(3)	1.18 (5)
Ru(1)–P(2)	1.83 (3)	C(4)–O(4)	1.17 (6)
Ru(1)–C(2)	1.80 (3)	C(5)–O(5)	1.16 (4)
Ru(2)–C(3)	1.83 (4)	C(6)–O(6)	1.17 (6)
Ru(2)–C(4)	1.82 (5)	C(7)–O(7)	1.15 (4)
Ru(2)–C(5)	1.83 (3)	C(8)–O(8)	1.19 (6)
Ru(3)–C(6)	1.82 (5)		

Ru(2)–Ru(1)–Ru(3)	59.6 (1)	P(1)–Ru(2)–C(5)	95 (1)
Ru(1)–Ru(2)–Ru(3)	63.5 (1)	C(3)–Ru(2)–C(4)	101 (2)
Ru(1)–Ru(3)–Ru(2)	56.9 (1)	C(3)–Ru(2)–C(5)	95 (2)
Ru(2)–Ru(1)–P(1)	52.1 (3)	C(4)–Ru(2)–C(5)	95 (2)
Ru(2)–Ru(1)–P(2)	164.1 (3)	Ru(1)–Ru(3)–C(6)	142 (1)
Ru(2)–Ru(1)–C(1)	87 (1)	Ru(1)–Ru(3)–C(7)	118 (1)
Ru(2)–Ru(1)–C(2)	99 (1)	Ru(1)–Ru(3)–C(8)	91 (2)
Ru(3)–Ru(1)–P(1)	72.3 (3)	Ru(1)–Ru(3)–C(10)	92 (1)
Ru(3)–Ru(1)–P(2)	114.3 (3)	Ru(2)–Ru(3)–C(6)	86 (1)
Ru(3)–Ru(1)–C(1)	147 (1)	Ru(2)–Ru(3)–C(7)	175 (1)
Ru(3)–Ru(1)–C(2)	93 (1)	Ru(2)–Ru(3)–C(8)	95 (2)
P(1)–Ru(1)–P(2)	112.8 (3)	Ru(2)–Ru(3)–C(10)	90 (1)
P(1)–Ru(1)–C(1)	87 (1)	C(6)–Ru(3)–C(7)	100 (2)
P(1)–Ru(1)–C(2)	151 (1)	C(6)–Ru(3)–C(8)	93 (2)
P(2)–Ru(1)–C(1)	97 (1)	C(6)–Ru(3)–C(10)	87 (2)
P(2)–Ru(1)–C(2)	95 (1)	C(7)–Ru(3)–C(8)	85 (2)
C(1)–Ru(1)–C(2)	94 (2)	C(7)–Ru(3)–C(10)	90 (2)
Ru(1)–Ru(2)–P(1)	53.7 (3)	C(8)–Ru(3)–C(10)	175 (2)
Ru(1)–Ru(2)–C(3)	153 (2)	Ru(1)–C(1)–O(1)	173 (4)
Ru(1)–Ru(2)–C(4)	98 (1)	Ru(1)–C(2)–O(2)	176 (3)
Ru(1)–Ru(2)–C(5)	103 (1)	Ru(2)–C(3)–O(3)	174 (4)
Ru(3)–Ru(2)–P(1)	75.1 (3)	Ru(2)–C(4)–O(4)	174 (4)
Ru(3)–Ru(2)–C(3)	97(1)	Ru(2)–C(5)–O(5)	175 (3)
Ru(3)–Ru(2)–C(4)	89 (1)	Ru(3)–C(6)–O(6)	175 (4)
Ru(3)–Ru(2)–C(5)	166 (1)	Ru(3)–C(7)–O(7)	172 (4)
P(1)–Ru(2)–C(3)	105 (1)	Ru(3)–C(8)–O(8)	167 (5)
P(1)–Ru(2)–C(4)	151 (1)		

The phosphinidene ligand interacts with all three metal atoms, being bonded to Ru(3) through the C(10) of the orthometalated ring, Ru(3)–C(10) = 2.13 (4) Å, and to Ru(2) and Ru(1) through P(1) which acts as a slightly asymmetrical bridge on the Ru(1)–Ru(2) edge, 2.813 (5) Å. This Ru(1)–Ru(2)–P(1) bridge is perpendicular to the metal triangle (dihedral angle = 90.5 (2)°). The orthometalated ring is almost perpendicular to the other phenyl (dihedral angle = 90 (1)°), and with the coplanar Ru(3) and P(1) atoms it is perpendicular to the metal triangle

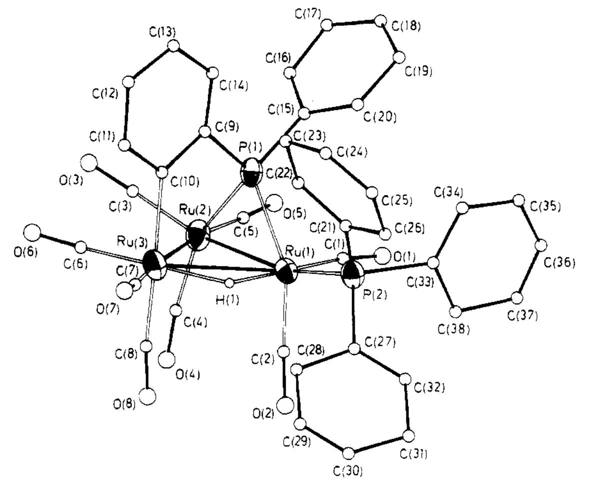
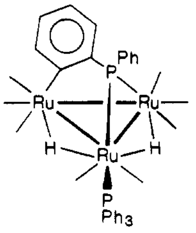


Figure 2. ORTEP drawing of the anion $[HRu_3(CO)_8(PPh_3)(PPhC_6H_4)]^-$ (3).

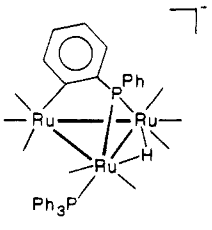
(dihedral angle = 91.8 (8)°), practically bisecting the Ru(1)–Ru(2) edge. The coordination around the Ru atoms is completed by eight terminal carbonyls and one PPh_3 ligand [bound to Ru(1)].

The cluster anion 3 reacts readily with phosphoric acid in THF solution to yield the corresponding neutral cluster $H_2Ru_3(CO)_8(PPh_3)(PPhC_6H_4)$ (4). Compound **4**, obtained in high yield as an air-stable, orange-red, crystalline material after chromatographic workup, is characterized in the mass spectrum by its molecular ion (*m/e* 976, relative to ^{101}Ru) and fragment ions due to successive loss of carbonyl ligands. The infrared spectrum of **4** displays seven ν(CO) bands in the region characteristic for terminal carbonyl ligands (Table I). On the basis of chemical shifts arguments the two ^{31}P NMR signals can be assigned unambiguously to the PPh_3 ligand (δ 27.4 ppm) and the μ_2-phosphinidene ligand (δ 130.2 ppm). Most informative for the constitution of **4** is the ^{1}H NMR spectrum which shows two hydride resonances: the signal at δ −14.01 ppm appears as a doublet of doublets of doublets due to ^{1}H–^{1}H homospin and two different ^{31}P–^{1}H heterospin couplings; in the signal at δ −17.22 ppm the ^{1}H–^{1}H, ^{31}P–^{1}H, and ^{1}H–^{31}P muliplicity degenerates to a doublet of virtual triplets. Because of the coupling pattern the two hydride bridges in **4** must be bonded to the ruthenium atom with the PPh_3 ligand.



4

With potassium triisobutylborohydride (potassium selectride) the neutral cluster **4** deprotonates to give the cluster anion **5** isomeric to **3**. Anion **5** can be isolated in the form of the tetraethylammonium salt as an orange, slightly air-sensitive crystalline material from dichloromethane–ether solutions. The cluster anions $[HRu_3(CO)_8(PPh_3)(PPhC_6H_4)]^-$ (**3** and **5**) differ in the position of the hydride bridge at the triangular metal framework. This difference is reflected in different IR and NMR data (Table I). The most noticeable difference is found in the ^{1}H NMR spectrum: whereas **3** gives rise to a doublet of doublets at δ −14.01 ppm, the hydride resonance of **5** appears at δ −17.76 ppm. This signal is also a doublet of doublets with one ^{31}P–^{1}H coupling constant being considerably larger [$J(^{31}P–^1H)$ = 9.4, 29.9 Hz] in accordance with a symmetric coupling through two ruthenium atoms.



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Scheme II. Isomerization of 3 to 5 via Protonation–Deprotonation

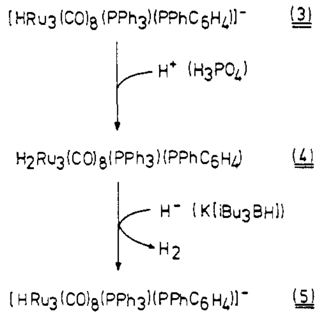

Table III. Experimental Data for the X-ray Diffraction Study on the Tetraethylammonium Salt of 3

mol formula	$C_{46}H_{45}NO_8P_2Ru_3$
mol wt	1105.02
cryst system	monoclinic
space group	$P2_1$
a, Å	13.250 (4)
b, Å	14.467 (4)
c, Å	12.667 (8)
β, deg	99.97 (2)
V, Å^3	2391 (2)
Z	2
D_{calcd}, g cm^{-3}	1.535
F(000)	1108
cryst dimens, mm	0.12 × 0.22 × 0.28
linear abs, cm^{-1}	10.31
diffractometer	Siemens AED
scan type	$\theta/2\theta$
scan speed, deg/min	2.5–12
scan width	$(\theta - 0.6) - (\theta + 0.6 + 0.346 \tan \theta)$
radiatn	Nb-filtered Mo Kα (λ v 0.71073 Å)
2θ range, deg	6–48
reflctns measd	$\pm h,k,l$
std reflctn	one measd after 50 reflctns
unique total data	3954
unique obsd data [$I > 2\theta(I)$]	1339
R	0.0576
R_w	0.0697

The neutral cluster **4** demonstrates that two Ru–Ru sites can be bridged by hydride ligands in this cluster system. Obviously, one of the hydride bridges is more exposed than the other; therefore it is better accessible to the attack of the sterically crowded selectride anion. This difference seems to account for the possibility for isomerizing anion **3** via protonation–deprotonation to anion **5**. A neutral cluster analogous to **4** has been previously reported by Mays et al.: $H_2Ru_3(CO)_9(PHC_6H_4)$ is accessible from the reaction of $Ru_3(CO)_{12}$ with phenylphosphine; contrary to **4** the two hydride ligands were assumed to bridge the two Ru–Ru sites not bridged by the phosphorus atom.[9]

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[9] Iwasaki, F.; Mays, M. J.; Raithby, P. R.; Taylor, P. C.; Wheatley, P. J. *J. Organomet. Chem.* **1981**, *213*, 185–206.

Table IV. Fractional Atomic Coordinates (×10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Ru(1)	2836 (2)	0	3427 (2)	C(18)	2449 (33)	3069 (33)	6845 (33)
Ru(2)	4193 (2)	1199 (3)	2624 (2)	C(19)	2745 (34)	2351 (36)	6694 (35)
Ru(3)	2279 (3)	800 (3)	1210 (2)	C(20)	2582 (31)	1905 (31)	5657 (34)
P(1)	2936 (7)	1621 (7)	3581 (7)	C(21)	197 (24)	−41 (29)	3997 (23)
P(2)	1456 (7)	−617 (8)	4105 (7)	C(22)	111 (27)	845 (31)	3503 (26)
O(1)	4351 (18)	−176 (22)	5477 (18)	C(23)	−869 (31)	1391 (31)	3334 (29)
O(2)	3476 (23)	−1835 (18)	2646 (23)	C(24)	−1675 (30)	881 (35)	3680 (31)
O(3)	4598 (26)	2934 (20)	1466 (25)	C(25)	−1559 (33)	57 (39)	4178 (31)
O(4)	5247 (26)	−252 (24)	1537 (27)	C(26)	−658 (30)	−501 (30)	4346 (30)
O(5)	5874 (20)	1415 (24)	4513 (21)	C(27)	962 (26)	−1742 (26)	3486 (27)
O(6)	2994 (29)	2085 (25)	−354 (28)	C(28)	758 (32)	−1725 (30)	2357 (34)
O(7)	216 (20)	366 (23)	−1 (27)	C(29)	367 (42)	−2571 (49)	1931 (43)
O(8)	3204 (34)	−915 (26)	424 (39)	C(30)	163 (46)	−3301 (45)	2454 (53)
C(1)	3770 (23)	−46 (32)	4672 (21)	C(31)	396 (41)	−3384 (41)	3604 (46)
C(2)	3241 (32)	−1083 (21)	2933 (30)	C(32)	788 (29)	−2506 (32)	4046 (31)
C(3)	4494 (38)	2259 (26)	1954 (38)	C(33)	1837 (27)	−884 (26)	5580 (27)
C(4)	4827 (37)	346 (28)	1915 (38)	C(34)	1514 (28)	−320 (27)	6344 (30)
C(5)	5252 (27)	1311 (38)	3752 (27)	C(35)	1939 (29)	−498 (30)	7419 (30)
C(6)	2755 (35)	1556 (30)	259 (34)	C(36)	2641 (32)	−1182 (32)	7655 (33)
C(7)	1042 (24)	490 (34)	428 (33)	C(37)	2978 (28)	−1746 (29)	6990 (30)
C(8)	2752 (48)	−245 (33)	633 (51)	C(38)	2582 (28)	−1622 (27)	5800 (29)
C(9)	1931 (24)	2357 (27)	2851 (26)	N(1)	3342 (26)	5609 (26)	1108 (26)
C(10)	1614 (27)	1993 (28)	1788 (28)	C(39)	3057 (45)	5135 (42)	2030 (35)
C(11)	802 (33)	2508 (34)	1157 (34)	C(40)	3163 (48)	5515 (42)	3117 (33)
C(12)	377 (35)	3330 (35)	1545 (38)	C(41)	3358 (39)	4930 (37)	201 (42)
C(13)	677 (32)	3615 (30)	2599 (34)	C(42)	2301 (41)	4473 (43)	−114 (47)
C(14)	1499 (30)	3086 (30)	3263 (30)	C(43)	2509 (37)	6329 (38)	703 (46)
C(15)	3213 (26)	2174 (25)	4905 (25)	C(44)	2721 (60)	6790 (52)	−281 (56)
C(16)	3890 (311)	2918 (30)	5139 (32)	C(45)	4342 (33)	6100 (37)	1330 (45)
C(17)	4015 (33)	3403 (33)	6101 (36)	C(46)	5211 (32)	5497 (47)	1804 (49)

Experimental Section

General Comments. All reactions were carried out under an atmosphere of purified nitrogene. Solvents were distilled from drying agents and deoxygenated prior to use. Preparative thin-layer chromatography was performed by using 20 × 20 cm plates coated with Merck silica gel 60 GF. Na[HRu$_3$(CO)$_{11}$] and [NEt$_4$][HRu$_3$(CO)$_{11}$] were prepared by a published procedure;[10,11] other reagents were commercially available. Nuclear magnetic resonance spectra were taken on a Bruker WP 80 or a Bruker WH 270 spectrometer. A Perkin-Elmer 580 instrument was used to record infrared spectra. Mass spectra were obtained with a Varian MAT CH7 instrument operating at 70 eV. Microanalyses were performed by using a Carlo Erba elementar analyzer 1106.

Preparation of [NEt$_4$][HRu$_3$(CO)$_8$(PPh$_3$)(PPhC$_6$H$_4$)] (Anion 3). To a solution of 0.5 mmol of [HRu$_3$(CO)$_{11}$]$^-$, prepared from 320 mg (0.5 mmol) of Ru$_3$(CO)$_{12}$ and 80 mg (2.0 mmol) of Na[BH$_4$] in 50 mL of THF,[10] was added 263 mg (1.0 mmol) of PPh$_3$. The solution was refluxed for 3 h; after removal of the solvent the residue was dissolved in 40 mL of methanol. After addition of 105 mg (0.5 mmol) of [NEt$_4$]Br the solution was concentrated to approximately 20 mL. The product, obtained by crystallization at ambient temperature, was recrystallized from a dichloromethane–ether solution and dried in vacuo: orange crystals; yield 475 mg (86%). Anal. Calcd for C$_{46}$H$_{45}$NO$_8$P$_2$Ru$_3$: C, 50.00; H, 4.10; N, 1.27. Found: C, 49.82; H, 4.21; N, 1.56.

Preparation of H$_2$Ru$_3$(CO)$_8$(PPh$_3$)(PPhC$_6$H$_4$) (4). [NEt$_4$][HRu$_3$(CO)$_8$(PPh$_3$)(PPhC$_6$H$_4$)] (anion **3**) (276 mg, 0.25 mmol) was dissolved in 30 mL of THF; 0.5 mL of concentrated phosphoric acid was added. The solution was stirred for 30 min and then concentrated to dryness; the residue was dissolved in 2 mL of dichloromethane and separated by preparative thin-layer chromatography using CH$_2$Cl$_2$/cyclohexane (2:3) as the elutant. The product was extracted from the brownish yellow band with dichloromethane and recrystallized from dichloromethane–pentane: dark yellow crystals; yield 203 mg (83%). Anal. Calcd for C$_{38}$H$_{28}$O$_8$P$_2$Ru$_3$: C, 46.78; H, 2.69. Found: C, 46.96; H, 2.64.

Preparation of [NEt$_4$][HRu$_3$(CO)$_8$(PPh$_3$)(PPhC$_6$H$_4$)] (Anion 5). To a THF solution of 98 mg (0.1 mmol) of H$_2$Ru$_3$(CO)$_8$(PPh$_3$)(PPhC$_6$H$_4$) (**4**) was added 1 mL of a 0.1 M solution of potassium selectride. The mixture was stirred at ambient temperature for 3 h. After removal of the solvent, the residue was taken into 10 mL of methanol. [NEt$_4$]Br (20 mg, 0.1 mmol) was added, and the solution was concentrated to about one-third of its volume. The product was obtained upon cooling to −30 °C, isolated, and dried in vacuo: yellow crystals; yield 70 mg (63%). Anal. Calcd for C$_{46}$H$_{45}$NO$_8$P$_2$Ru$_3$: C, 50.00; H, 4.10; N, 1.27. Found: C, 50.01; H, 4.19; N, 1.34.

Spectroscopic Characterization of the Intermediate Cluster Anions 1 and 2. Infrared spectra were recorded by using a solution of 570 mg (0.5 mmol) of [NEt$_4$][HRu$_3$(CO)$_{11}$] and 131 mg (0.5 mmol) of PPh$_3$ in 50 mL of THF kept at 0 °C. The NMR measurements were done with a solution of 57 mg (0.05 mmol) of [NEt$_4$][HRu$_3$(CO)$_{11}$] in 1 mL of THF-d_8; for the ^{13}C NMR spectra a ^{13}C-enriched sample of Ru$_3$(CO)$_{12}$[11] was employed.

X-ray Data Collection, Structure Determination, and Refinement for [NEt$_4$][HRu$_3$(CO)$_8$(PPh$_3$)(PPhC$_6$H$_4$)] (Anion 3). Single crystals of the tetraethylammonium salt of **3** were obtained by recrystallization from methanol. All crystals were of small size and of poor quality. An orange-red prismatic crystal was selected and mounted on a Siemens AED diffractometer. The crystallographic data are summarized in Table III. Unit-cell parameters were obtained from the θ values of 30 carefully centered reflections, having $9 < \theta < 15°$. The data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[12] The structure amplitudes were obtained after usual Lorentz and polarization reduction,[13] correction for absorption effects having been ignored because of the very low absorbance of the sample. Only the observed reflections were used in the structure solution and refinement.

The structure was solved by direct and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for the Ru and P atoms only,

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(13) Data reduction, structure solution, and refinement were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio, Bologna) and on the GOULD-SEL 32/77 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 system of crystallographic computer programs (Sheldrick, G. M. Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

because of the low number of observed reflections. The tetraethylammonium cation was found a little disordered, as indicated by the high thermal parameters of the carbon atoms and by some residual peaks close to the carbon atoms. The hydride was clearly localized in the final difference Fourier. All hydride atoms of the anion were placed at their geometrically calculated positions and introduced in the final structure factor calculation, together with the hydridic one, with fixed isotropic thermal parameters. The final cycles of refinement were carried out on the basis of 265 variables; after the last cycle, no parameters shifted by more than 0.7 esd. The biggest remaining peaks in the final difference map, close to the Ru atoms and the ethyl carbon atoms, were equivalent to about 0.6 e/Å^3. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the K and g values were 0.593 and 0.0059, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 14.

The final atomic coordinates for the non-hydrogen atoms are given in Table IV. The atomic coordinates for the hydrogen atoms of the anion and the hydridic one are given in Table SI; thermal parameters for the non hydrogen atoms are given in Table SII. In independent cycles of refinement the coordinates $-x$, $-y$, $-z$ were used for the non-hydrogen atoms because of the acentric space group. No improvement in the R value was obtained $|R(x, y, z) = R(-x, -y, -z) = 0.0574|$. The former model was maintained and the reported data refer to this model.

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Registry No. [**1**][NEt$_4$], 119296-15-0; [**2**][NEt$_4$]$_2$, 119296-17-2; [**3**][NEt$_4$], 119325-58-5; **4**, 119296-18-3; [**5**][NEt$_4$], 119296-20-7, 71936-71-5.

Supplementary Material Available: Table S1, coordinates for the hydrogen atoms of the anion, Table S2, thermal parameters for the non-hydrogen atoms, and tables of atomic coordinates, crystal data, bond distances and angles, and least-squares planes (22 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Novel Physical and Chemical Properties of Acyclic, Conjugated Dienes Coordinated to Cp'Mo(NO) Groups [Cp' = η^5-C_5H_5 (Cp) or η^5-C_5Me_5 (Cp*)][1,2]

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Reduction of [Cp'Mo(NO)I$_2$]$_2$ (Cp' = η^5-C_5H_5 (Cp) or η^5-C_5Me_5 (Cp*)) by sodium amalgam in THF at −20 °C in the presence of acyclic, conjugated dienes affords novel Cp'Mo(NO)(η^4-*s-trans*-diene) complexes in isolated yields of ~10–60%. When the diene is 2,3-dimethylbutadiene, Cp'Mo(NO)(η^4-*cis*-2,3-dimethylbutadiene) product complexes are also isolable in addition to the *trans*-diene-containing isomers. However, these *cis*-diene compounds are kinetic products and convert in solutions irreversibly to the isomeric *trans*-diene complexes. Treatment of [CpMo(NO)I$_2$]$_2$ with 2 equiv of $C_4H_6Mg(THF)_2$ in Et_2O results in the precipitation of the adduct CpMo(NO)I$_2$·C_4H_6Mg·$^1/_2$(Et_2O) whose physical properties indicate that it contains an Mo–NO→Mg isonitrosyl linkage. Thermolysis of the adduct in THF at room temperature for 5 days produces CpMo(NO)(η^4-*trans*-C_4H_6) in 38% yield. A detailed analysis of the ^{1}H and ^{13}C NMR spectroscopic properties of the 14 new η^4-diene-containing complexes isolated during this work has been carried out. This analysis has established unequivocally the different conformations of the diene ligands in these "piano stool" organometallic molecules. Furthermore, it has provided evidence that the *cis*- and *trans*-diene ligands are bonded to the Cp'Mo(NO) groups in a similar manner, the bonding rationale in MO terms involving substantial diene π_2→Mo and Mo→diene π_3^* electron donation in both cases. The Mo–η^4-*trans*-diene linkage in CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene) is relatively kinetically inert to substitution, converting only slowly to CpMo(NO)(L)(η^2-diene) species when exposed to Lewis bases, L, such as PMePh$_2$, PMe$_3$, or CO, the latter at 60 psig in hexanes at 20 °C for 5 days.

Introduction

Many monomeric transition-metal complexes containing acyclic, conjugated dienes have been prepared since the first report of (η^4-C_4H_6)Fe(CO)$_3$ appeared in 1930.[4] Several of these complexes, particularly those containing iron, have found interesting applications in organic synthesis.[5] In the vast majority of these complexes, the diene ligand is attached to a central metal in the well-known, planar η^4-*s-cis* manner.[6] The only examples to date of η^4-*s-trans*

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