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Site-Selective Substitution Reactions and Isomerizations in Tetrahedral MCo_3 Carbonyl Clusters (M = Fe, Ru) with N, P, S, and Te Donor Ligands. Crystal Structures of $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ and $HRuCo_3(CO)_9(PMe_2Ph)_3$

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We report on the influence of the metals and of the ligands on site-selective substitution reactions with various two-electron donor ligands. The reaction between the tetrahedral mixed-metal cluster $HRuCo_3(CO)_{11}(PMe_2Ph)$ (**1**) and PMe_2Ph has led selectively to the disubstituted cluster $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (**2a**) in which the phosphines are bound to cobalt atoms [isomer Co,Co]. This cluster spontaneously transforms in CH_2Cl_2 into the isomer **2b** in which a phosphine is bound to ruthenium [Co,Ru]. Reaction of **2a** with PMe_2Ph occurs via first isomerization in **2b**, which instantly yields $HRuCo_3(CO)_9(PMe_2Ph)_3$ [Co,Co,Ru] (**3**). The latter is best prepared by the reaction of **1** with 2 equiv of PMe_2Ph in the presence of Me_3NO. Clusters containing different phosphine ligands have also been prepared. In contrast to the reactions of PMe_2Ph with the clusters $HRuCo_3(CO)_{11}(E)$ (E = SMe_2, $SeMe_2$, $TePh_2$) in which the Ru-bound chalcogenide ligand is displaced by the phosphine without formation of a disubstituted cluster, the reaction of **1** with $TeMe_2$ produced $HRuCo_3(CO)_{10}(PMe_2Ph)(TeMe_2)$ (**4**) in good yield. Reaction of **1** with SEt_2 afforded a mixture containing the disubstituted clusters $HRuCo_3(CO)_{10}(PMe_2Ph)(SEt_2)$ in the form of two isomers, [Co,Co] (**5a**) and [Co,Ru] (**5b**). In the presence of Me_3NO, mainly **5b** was formed. In $HRuCo_3(CO)_{10}(NMe_3)(PMe_2Ph)$ (**6a**), which was obtained from **1** and Me_3NO, the amine ligand is readily displayed by SEt_2 to give **5a** selectively and in quantitative yields. Spectroscopic IR [ν(CO)] and ^1H and ^{59}Co NMR data are presented. Comparative studies have been performed with $HFeCo_3(CO)_{11}$(phosphine): reactions with phosphine, amine, or thioether ligands afford only the [Co,Co] disubstituted clusters. Reaction from $HFeCo_3(CO)_{12-n}L_n$ (n = 0–2) never led to substitution at iron. Clusters **2b** and **3** have been structurally characterized by X-ray diffraction: $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (**2b**) crystallizes in the space group $P2_1/c$, monoclinic, with a = 17.69(1) Å, b = 14.275(7) Å, c = 12.518(7), β = 97.64(5)°, and Z = 4, and $HRuCo_3(CO)_9(PMe_2Ph)_3$ (**3**) crystallizes in the space group $P2_1/c$, monoclinic, with a = 10.927(5) Å, b = 21.275(5) Å, c = 16.096(3), β = 94.65(3)°, and Z = 4.

Introduction

Previous studies on the substitution chemistry of mixed-metal, tetrahedral carbonyl clusters of the type $HMCo_3(CO)_{12}$ (M = Fe, Ru) have shown that the terminal cobalt carbonyls are more prone to nucleophilic substitution by two electron donor ligands than the carbonyls bound to the apical metal M = Fe, Ru.[1,2] Only few exceptions have been reported where the ligand L in $HRuCo_3(CO)_{11}L$ has

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(1) (a) Cooke, C. G.; Mays, M. J. *J. Chem. Soc. Dalton Trans.* **1975**, 455. (b) Hidai, M.; Matsuzaka, H.; Koyasu, Y.; Uchida, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1451. (c) Matsuzaka, H.; Kodama, T.; Uchida, Y.; Hidai, M. *Organometallics* **1988**, *7*, 1608. (d) Pursiainen, J.; Ahlgren, M.; Pakkanen, T. A.; Valkonen, J. *J. Chem. Soc., Dalton Trans.* **1990**, 1147. (e) Braunstein, P.; Rosé, J.; Granger, P.; Raya, J.; Bouaoud, S.-E.; Grandjean, D. *Organometallics* **1991**, *10*, 3686.

(2) Braunstein, P.; Mourey, L.; Rosé, J.; Granger, P.; Richert, T.; Balegroune, F.; Grandjean, D. *Organometallics* **1992**, *11*, 2628.

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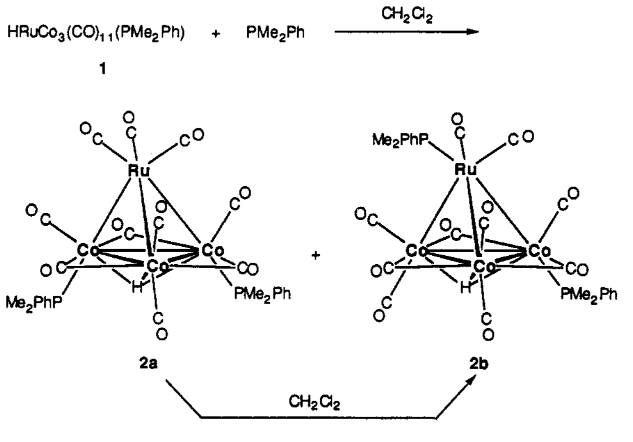
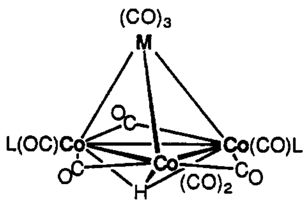
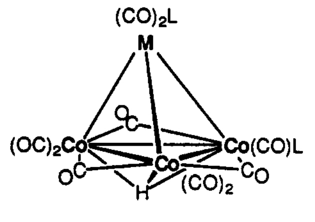
Scheme 1



been established by X-ray diffraction to be bound to Ru,[3] and only in the trisubstituted cluster $HFeCo_3(CO)_9(PMe_2Ph)_3$ has a ligand L replaced a Fe-bound carbonyl ligand.[4] It therefore appeared interesting to investigate disubstituted clusters belonging to this family and examine the role of the apical metal M and of the two electron donor ligands L and L′, in particular when L ≠ L′, on the substitution pattern. In the following, the isomers in which each of these ligands is bound to a different cobalt atom will be referred to as [Co,Co], whereas those in which the ligands are bound to a cobalt atom and the metal M will be referred to as [Co,M].



[Co, Co] isomer



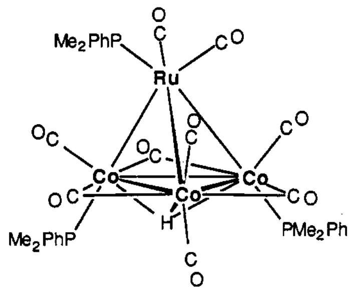
[Co, M] isomer

Results and Discussion

Reactions of $HRuCo_3(CO)_{11}(PMe_2Ph)$ (1) with Donor Ligands. Reactions with Phosphines. Reaction of $HRuCo_3(CO)_{11}(PMe_2Ph)$ (1) with PMe_2Ph (1:1 molar ratio) afforded under ambient conditions $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ [Co,Co] (**2a**) which contains two cobalt-coordinated axial phosphines. No [Co,Ru] isomer **2b** was observed after 1 h reaction time. The disubstituted derivative was also obtained by the reaction of $HRuCo_3(CO)_{12}$ with 2 equiv. PMe_2Ph, which proceeds via very rapid formation of the monosubstituted cluster (TLC evidence). An interesting feature is that the isomer [Co,Co] (**2a**) first formed completely isomerized after standing in CH_2Cl_2 overnight into [Co,Ru] (**2b**), in which one phosphine has migrated to ruthenium (Scheme 1). With other phosphine ligands, disubstituted clusters may also be obtained and the preferred isomer depends on the nature of the phosphine: in the case of PPh_3 only the [Co,Co] isomer was isolated whereas with, e.g., $PPhH_2$ or PPh_2H, a mixture of isomers was obtained.

Isolated **2a** reacted over few hours with 1 equiv of PMe_2Ph in CH_2Cl_2 to give quantitatively $HRuCo_3(CO)_9(PMe_2Ph)_3$ [Co,Co,Ru] (**3**) which contains two basal (on Co) and one apical (on Ru) phosphines. The solid-state structure is described below. In view of the isomerization of **2a** in **2b**, we studied independently the reaction of **2b** with PMe_2Ph. It instantly yielded **3**, suggesting that the reaction of **2a** with PMe_2Ph occurs first via isomerization in **2b**. A comparison between the reactions of **2b** with PMe_2Ph with the weaker nucleophile PPh_3 showed that under similar conditions, the former reaction is instantaneous whereas the latter yields ca. 10 % of $HRuCo_3(CO)_9(PMe_2Ph)_2(PPh_3)$ [Co,Ru,Co(PPh_3)] after 5 days. On the other hand, the reaction of $HRuCo_3(CO)_{10}(PPh_3)_2$ [Co,Co] with excess PPh_3 afforded, after 24 h at room temperature, some $HRuCo_3(CO)_{10}(PPh_3)_2$ [Co,Ru] and $HRuCo_3(CO)_9(PPh_3)_3$ [Co,Co,Ru]. After 5 days, the conversion is ca. 50%, and these products are obtained in a 1:3 ratio. This is consistent with the fact that, for a given entering group (PPh_3), substitution of a cobalt-bound carbonyl ligand is more difficult in the more electron-rich cluster. This trisubstituted cluster **3** is in fact best prepared by the reaction of 1 with 2 equiv of PMe_2Ph in the presence of Me_3NO (quantitative yield after 0.5 h reaction) (eq 1).

$$1 + 2\,PMe_2Ph + Me_3NO \xrightarrow[-CO,\,-CO_2]{CH_2Cl_2}$$



(1)

3

This reaction proceeds by first rapid and quantitative formation of the kinetic isomer **2a** which instantly reacts with the amine oxide and the second equivalent of PMe_2Ph to give the stable trisubstituted cluster **3**. After a longer reaction time, **3** subsequently transforms into species not yet fully characterized (see Experimental Section). In this case, the spontaneous isomerization of the [Co,Co] isomer (**2a**) into the [Ru,Co] isomer (**2b**) appears too slow to represent a significant pathway in the overall reaction. However, we shall see below with chalcogenide ligands that reaction of **2a** with Me_3NO most likely leads to a cluster of type **A**, rather than of type **B**, which rapidly reacts with the third equivalent of phosphine with displacement of the Co-bound amine ligand. A related amine displacement reaction has been described with $HRuCo_3(CO)_{11}(NMe_3)$ and various phosphine ligands, which led to the cobalt-substituted clusters $HRuCo_3(CO)_{11}$(phosphine) in quantitative yields.[2] Similarly, intermediate **A** would also account for the reaction of **2b** with $PCyH_2$ in the presence of Me_3NO. It yielded pure $HRuCo_3(CO)_9(PMe_2Ph)_2(PCyH_2)$, which has a phosphine ligand bound to Ru. In solution, $HRuCo_3(CO)_9(PMe_2Ph)_2(PCyH_2)$ transforms slowly with formation of **3**, but the fate of the $PCyH_2$ ligand is not known.

Reactions with Chalcogenides. The reaction of 1 with $TeMe_2$ produced $HRuCo_3(CO)_{10}(PMe_2Ph)(TeMe_2)$ (**4**) in good yield. The same product was also obtained in 58%

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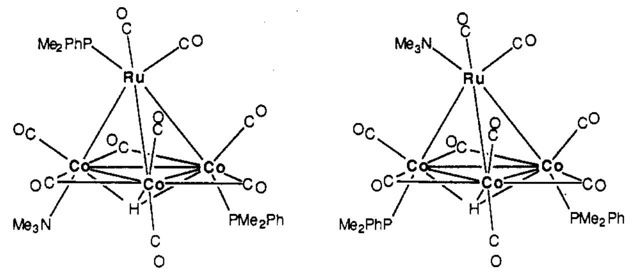
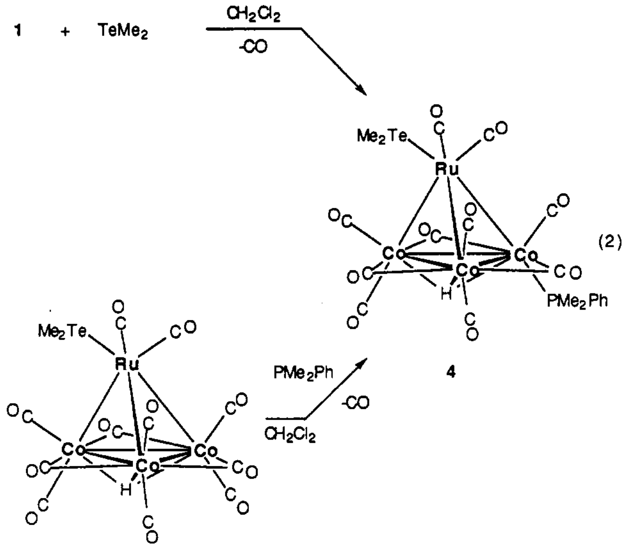
[3] Rossi, S.; Pursiainen, J.; Pakkanen, T. A. *J. Organomet. Chem.* **1990**, *397*, 81.

[4] Bartl, K.; Boese, R.; Schmid, G. *J. Organomet. Chem.* **1981**, *206*, 331.

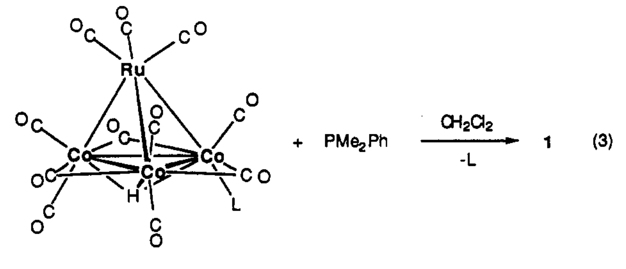


A B

yield from the reaction of the structurally characterized Ru-bound telluride cluster $HRuCo_3(CO)_{11}(TeMe_2)$ with PMe_2Ph (eq 2), strongly suggesting that the telluride ligand in 4 is bound to the apical ruthenium site. The latter reaction contrasts with those of PMe_2Ph with $HRuCo_3(CO)_{11}(SMe_2)$, $HRuCo_3(CO)_{11}(SeMe_2)$ or $HRuCo_3(CO)_{11}(TePh_2)$ in which the cobalt-bound chalcogenide ligand L is easily replaced by PMe_2Ph, without formation of a disubstituted cluster (eq 3). Reaction 3 is rapid at room temperature as well as a 0 °C. Both SMe_2 and $SeMe_2$ are replaced more easily than a carbonyl ligand. The SMe_2 ligand is also easily replaced by carbon monoxide, although in the preparation of $HRuCo_3(CO)_{11}(SR_2)$ (R = Me, Et) or $HRuCo_3(CO)_{11}(SeMe_2)$ the chalcogenide ligand (present in excess) has replaced a carbonyl group.



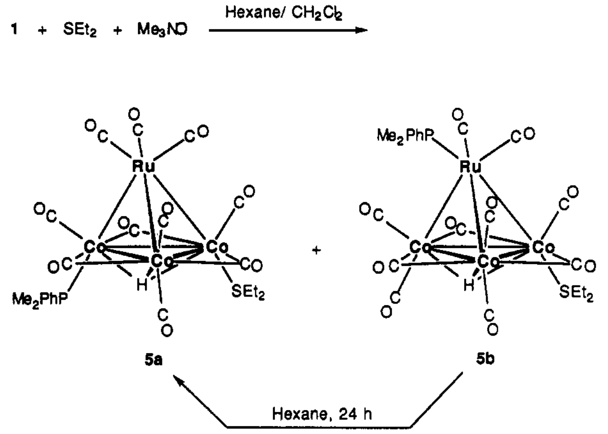
4



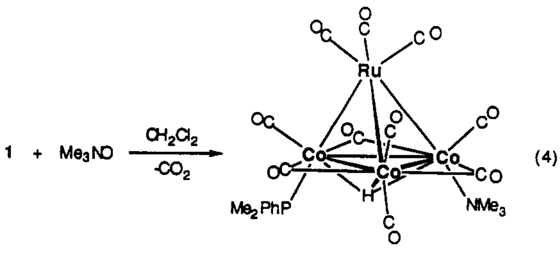
L = SMe_2, $SeMe_2$, $TePh_2$

No reaction occurred between 1 and SEt_2 in hexane at room temperature, but under reflux, a complex mixture was obtained in which the disubstituted cluster $HRuCo_3(CO)_{10}(PMe_2Ph)(SEt_2)$ is present in the form of two isomers of which the [Co,Co] isomer **5a** could be independently characterized. The second isomer **5b** most certainly has a substituent on ruthenium, although its exact nature could not be ascertained in the absence of X-ray quality crystals. When 1 was reacted with 1 equiv of SEt_2 in a mixture of hexane/CH_2Cl_2 (5:1) in the presence of Me_3NO, a clean reaction yielded mainly brown **5b**, and a smaller yield of violet **5a** (Scheme 2). The proportion of **5a** increases with increasing reaction times. The nature of these isomers, i.e., which ligand is bound to which metal center, was established on the following grounds. Whereas **5b** has IR ν(CO) and ^1H NMR (hydrido signal) spectroscopic characteristics similar to those of **2b**, the data for **5a** are closely related to those of **2a** (see Table 1). Both isomers show in the ^{59}Co NMR spectrum a resonance at ca. δ −1900 which is typical in this family of clusters for a S-substituted cobalt nucleus.[2] The spectrum of **5a** contains in addition two distinct resonances in a 1:1 ratio at δ −2640 and δ −2710 which correspond to the Co–(PMe_2Ph) and Co–(CO) nuclei, respectively. In the spectrum of **5b**, only one additional resonance is observed at δ −2250 which corresponds to the two equivalent Co–(CO) nuclei. When pure **5b** was dissolved in hexane, it isomerized to **5a** within ca. 24 h (ca. 80% conversion) (Scheme 2) while some decomposition began to occur with liberation of SEt_2 and formation of 1 (some CO liberated by decomposition occupies the coordination site left vacant by SEt_2).

Scheme 2



It is noteworthy that from the reaction of 1 with Me_3NO in CH_2Cl_2, we could only characterize the isomer of $HRuCo_3(CO)_{10}(NMe_3)(PMe_2Ph)$ (**6a**) in which both substituents are bound to cobalt atoms (eq 4). This cluster loses its NMe_3 ligand more rapidly than **5a** looses its thioether ligand, in agreement with previous findings about the lability of the Co–amine bond.[1e] As expected, the amine ligand of **6a** is rapidly displaced by SEt_2 (slight excess in CH_2Cl_2) to selectively give **5a** in quantitative yields, again without occurrence of **5b**. Therefore, amine substitution by SEt_2 does not induce any isomerization. From these results, it appears reasonable to suggest that the reaction of 1 with Me_3NO occurs via a short-lived



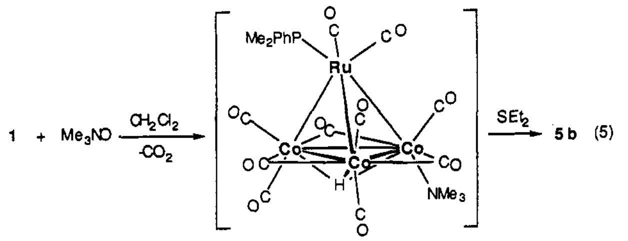
6a

Table 1. Selected Physical and Spectroscopic Data

cluster		color in solution	IR	NMR	
formula	no.		ν(CO), cm^{-1} (CH_2Cl_2)	δ(^{1}H)(μ_3-H)	δ(^{59}Co) ($\Delta\nu_{1/2}$, Hz)[a]
$HRuCo_3(CO)_{11}(PMe_2Ph)$	**1**	wine red	2081 s, 2042 vs, 2034 sh, 2009 vs, 1862 m, 1845 m	−20.2	−2745 (3500) (Co–CO) −2715 (2800) (Co–P)
$HRuCo_3(CO)_{10}(PMe_2Ph)_2$	**2a**	violet	2065 s, 2014 s, 1998 vs, 1842 m, 1824 m	−20.1	−2690 (3300) (Co–CO) −2580 (3300) (Co–P)
	2b	red brown	2048 m, 2013 vs, 1966 sh, 1851 m, 1843 m	−18.3	−2750 (2900) (Co–CO) −2604 (6950) (Co–P)
$HRuCo_3(CO)_9(PMe_2Ph)_3$	**3**	dark violet	2019 s, 1987 vs, 1955 s, 1822 s, 1810 sh	−18.8	−2620 (3700) (Co–CO + Co–P)
$HRuCo_3(CO)_{10}(PMe_2Ph)(TeMe_2)$	**4**	dark red	2047 w, 2010 vs, 1966 m, 1844 m	−18.4	−2755 (3900) (Co–CO) −2600 (3200) (Co–P)
$HRuCo_3(CO)_{10}(PMe_2Ph)(SEt_2)$	**5a**	violet	[b]2072 s, 2023 s, 1997 vs, 1843 m, 1822 m	−20.1	−2710 (5250) (Co–CO) −2640 (4200) (Co–P) −1900 (2600) (Co–S)
	5b	brown	[b]2048 m, 2017 s, 2011 vs, 1965 m, 1860 m, 1845 m	−18.4	−2550 (2100) (Co–CO + Co–P) −1900 (3600) (Co–S)
$HRuCo_3(CO)_{10}(PMe_2Ph)(NMe_3)$	**6a**	violet	2070 s, 2024 s, 1992 vs, 1861 w, 1831 m, 1814 m	−21.0	−2714 (3100) (Co–CO) −2553 (3600) (Co–P) −956 (4000) (Co–N)

[a] Measured at 298 K in $CDCl_3$; sample concentrations in the range 1–2 × 10^{-2} mol/L; reference is $K_3[Co(CN)_6]$ in D_2O; the line widths are not meaningful since they contain relaxation effects and coupling constants. [b] Recorded in hexane.

intermediate **6b** (not evidenced in the reaction of eq 4) in which the phosphine has temporarely migrated to Ru. This situation is then frozen in the presence of SEt_2 which displaces the amine ligand, leading to **5b** (eq 5). The latter subsequently isomerizes to **5a** (Scheme 2). This reaction sequence is also consistent with the lack of observation in all our studies of any Ru-bound amine ligand in these clusters. A similar behavior of **2a** with Me_3NO would account for the formation of a trisubstituted N,P,P cluster which, in the presence of PMe_2Ph, affords the phosphine cluster **3** described above.



6b

For comparison, we investigated some reactions of tetrahedral clusters of the type $HFeCo_3(CO)_{11}$(phosphine). Addition of 1 equiv of a two electron donor ligand such as a phosphine, an amine or a thioether afforded the corresponding disubstituted cluster, but only the [Co,Co] derivatives were observed. It is interesting to remember that the trisubstituted cluster $HFeCo_3(CO)_9(PMe_2Ph)_3$ has been synthesized under conditions similar to ours and found to have a phosphine ligand attached to each cobalt center.[1a] However, another isomer which is the Fe analog of **3** has been structurally characterized: it was prepared in low yields (2.8%) by the thermal reaction of $FeCl_3$ with $Na[Co(CO)_4]$ in diethyl ether for 1 day, followed by the addition of excess PMe_2Ph.[4] This synthetic procedure strongly suggests that $[FeCo_3(CO)_{12}]^-$ was first formed and reacted then with PMe_2Ph with a different site-selectivity than $HFeCo_3(CO)_{12}$. This explanation is supported by our recent findings that $[RuCo_3(CO)_{12}]^-$ reacts with PPh_3 to give only $[RuCo_3(CO)_{10}(PPh_3)_2]^-$ [Co,Ru], which on protonation affords $HRuCo_3(CO)_{10}(PPh_3)_2$ [Co,Ru].[5] Obviously, the electron density in the basal plane of the $[MCo_3(CO)_{12}]^-$ anions favors the [Co,M] isomer over the [Co,Co] isomer. This provides an interesting contrast with the reaction from $HFeCo_3(CO)_{12-n}L_n$ (n = 0–2) which never led to substitution at iron.

For the triphosphine tetrahedral clusters, ^{59}Co NMR does not allow a clear structural identification since the [Co,Co,Ru] isomers surprisingly gives rise to a singlet resonance, as would also be anticipated for a [Co,Co,Co] isomer. X-ray diffraction remains therefore the only method to ascertain their structure. This is even more so when the question arises of the axial or equatorial position of the ligands in the Co_3 base. Note for example that the phosphite ligands in $HFeCo_3(CO)_9[P(OMe)_3]_3$ are all axial[6] whereas in $Ir_4(CO)_9(PPh_3)_3$ the phosphine ligands occupy one axial and two equatorial sites.[7]

This work emphasizes the importance of the sequence of introduction of the ligands for the selective synthesis of polysubstituted carbonyl clusters. However, more work is needed before systematic trends can be identified and a rationalization of this chemistry suggested.

Crystal Structures of $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (2b) and $HRuCo_3(CO)_9(PMe_2Ph)_3$ (3). The molecular structures of **2b** and **3** have been determined by X-ray diffraction and are shown in Figures 1 and 2. Selected bond lengths and bond angles are given in Tables 2 and 3. The substitution reactions maintain the basic cluster core and the three bridging carbonyls between the cobalt atoms. Both clusters contain one phosphine ligand bound to Ru, trans to a cobalt–phosphorus bond. The metal–metal distances in both clusters are in the range found in other $RuCo_3$ tetrahedral clusters. Note however that substitution at the Ru apex tends to increase the Ru–Co bonds: they range from 269.0(3) to 273.9(3) pm in **2b**, from 267.7(2) to 270.6(2) pm in **3**, and from 264.0(2) to 265.6(2) pm in $HRuCo_3(CO)_{10}(PPh_3)_2$ [Co,Co].[8] The Co–P distances are very similar to the values found in $HFeCo_3(CO)_{11}(PPh_2H)$ [222.3(1) pm][1e] but slightly shorter than in $HRuCo_3(CO)_{11}(PPh_3)$ [226.1(5) pm].[1c] The Ru–P distances are also similar in the two clusters and compare

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[5] Braunstein, P.; Rosé, J.; Xu, M. Unpublished results.

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[7] Albano, V.; Bellon, P.; Scatturin, V. *Chem. Commun.* **1967**, 730.

[8] Pursiainen, J.; Pakkanen, T. A. *J. Organomet. Chem.* **1985**, *290*, 85.

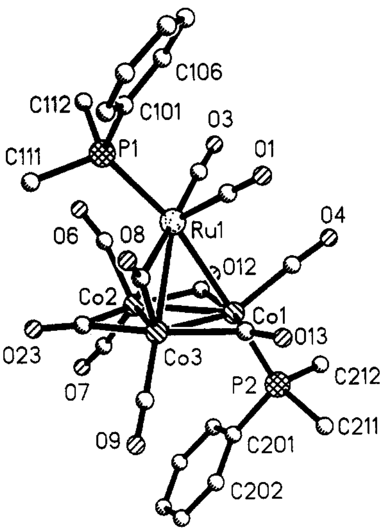

Figure 1. View of the molecular structure of $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (**2b**) with the atom labeling scheme. The hydrogen atom μ_3-bonded to the Co_3 face was not located by X-ray methods.

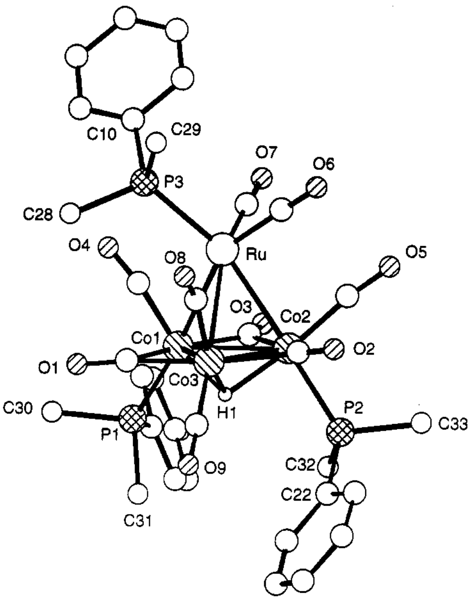

Figure 2. View of the molecular structure of $HRuCo_3(CO)_9(PMe_2Ph)_3$ [Co,Co,Ru] (**3**) with the atom labeling scheme.

with the mean value of 234.2 pm found for Ru–PMe_2Ph distances.[9] It is noteworthy than in both structures, the terminal carbonyls C(6)O(6) and C(8)O(8) are slightly bent toward the Ru atom [Co–C–O angles in the range 156(1)–169.6(7)°]. This appears to be due to the more electron-rich nature of the phosphine-substituted Ru atom since these ligands are linear in the clusters $HRuCo_3(CO)_{11}(L)$ (L = NMe_3, SMe_2, PPh_3).[1c–e] The arrangement of the phosphine ligands in **3** is similar to that in $HFeCo_3(CO)_9(PMe_2Ph)_3$[4] but differs from that in $HFeCo_3(CO)_9[P(OMe)_3]_3$.[6] It appears that both electronic and steric effects determine the metalloselectivity of substitution reactions and the ligand arrangement in substituted tetrahedral clusters. The hydridic ligand of **2b** could not be located by X-ray diffraction, in contrast to that of **3**. The Co–H distances in the latter [in the range 170(6)–172(6) pm] are not significantly different from those in $HFeCo_3(CO)_9[P(OMe)_3]_3$ [173.4(3) pm].[6]

Table 2. Selected Bond Distances (pm) and angles (deg) for $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (2b)

Bond Distances			
Ru(1)–Co(1)	273.9(3)	Co(1)–C(12)	194(2)
Ru(1)–Co(2)	269.8(3)	Co(1)–C(13)	193(2)
Ru(1)–Co(3)	269.0(3)	Co(2)–Co(3)	248.6(4)
Ru(1)–P(1)	236.7(5)	Co(2)–C(6)	178(2)
Ru(1)–C(1)	190(2)	Co(2)–C(7)	177(2)
Ru(1)–C(3)	190(2)	Co(2)–C(12)	197(2)
Ru(1)–C(8)	253(2)	Co(2)–C(23)	197(2)
Co(1)–Co(2)	250.6(4)	Co(3)–C(8)	181(2)
Co(1)–Co(3)	249.6(4)	Co(3)–C(9)	175(2)
Co(1)–P(2)	223.9(5)	Co(3)–C(13)	203(2)
Co(1)–C(4)	180(2)	Co(3)–C(23)	196(2)
Bond Angles			
Co(1)–Ru(1)–Co(2)	54.9(1)	Co(3)–Co(2)–C(7)	127.3(6)
Co(1)–Ru(1)–Co(3)	54.7(1)	Co(1)–Co(2)–C(12)	49.6(5)
Co(2)–Ru(1)–Co(3)	55.0(1)	Co(3)–Co(2)–C(12)	109.5(5)
Co(1)–Ru(1)–P(1)	167.7(1)	Co(1)–Co(2)–C(23)	110.5(5)
Co(2)–Ru(1)–P(1)	114.8(1)	Co(3)–Co(2)–C(23)	50.6(5)
Co(3)–Ru(1)–P(1)	114.8(1)	Ru(1)–Co(3)–Co(1)	63.6(1)
Co(1)–Ru(1)–C(1)	97.1(5)	Ru(1)–Co(3)–Co(2)	62.7(1)
Co(2)–Ru(1)–C(1)	149.7(5)	Co(1)–Co(3)–Co(2)	60.4(1)
Co(3)–Ru(1)–C(1)	101.1(5)	Ru(1)–Co(3)–C(8)	65.1(6)
Co(1)–Ru(1)–C(3)	96.8(5)	Co(1)–Co(3)–C(8)	119.6(6)
Co(2)–Ru(1)–C(3)	101.5(5)	Co(2)–Co(3)–C(8)	117.6(6)
Co(3)–Ru(1)–C(3)	149.5(5)	Ru(1)–Co(3)–C(9)	166.6(6)
Co(1)–Ru(1)–C(8)	90.3(4)	Co(1)–Co(3)–C(9)	125.2(6)
Co(2)–Ru(1)–C(8)	89.7(4)	Co(2)–Co(3)–C(9)	129.5(6)
Co(3)–Ru(1)–C(8)	40.5(4)	Co(1)–Co(3)–C(13)	49.1(5)
Ru(1)–Co(1)–Co(2)	61.7(1)	Co(2)–Co(3)–C(13)	109.5(5)
Ru(1)–Co(1)–Co(3)	61.6(1)	Co(1)–Co(3)–C(23)	111.3(5)
Co(2)–Co(1)–Co(3)	59.6(1)	Co(2)–Co(3)–C(23)	50.9(5)
Ru(1)–Co(1)–P(2)	176.0(2)	Ru(1)–C(1)–O(1)	179(1)
Co(2)–Co(1)–P(2)	114.6(2)	Ru(1)–C(3)–O(3)	178(2)
Co(3)–Co(1)–P(2)	118.6(2)	Co(1)–C(4)–O(4)	176(2)
Ru(1)–Co(1)–C(4)	84.9(6)	Co(2)–C(6)–O(6)	161(2)
Co(2)–Co(1)–C(4)	133.2(6)	Co(2)–C(7)–O(7)	174(2)
Co(3)–Co(1)–C(4)	132.8(6)	Ru(1)–C(8)–Co(3)	74.4(7)
Co(2)–Co(1)–C(12)	50.8(5)	Ru(1)–C(8)–O(8)	129(1)
Co(3)–Co(1)–C(12)	110.3(5)	Co(3)–C(8)–O(8)	156(2)
Co(2)–Co(1)–C(13)	112.4(6)	Co(3)–C(9)–O(9)	175(2)
Co(3)–Co(1)–C(13)	52.8(6)	Co(1)–C(12)–Co(2)	79.6(7)
Ru(1)–Co(2)–Co(1)	63.4(1)	Co(1)–C(12)–O(12)	142(1)
Ru(1)–Co(2)–Co(3)	62.3(1)	Co(2)–C(12)–O(12)	138(1)
Co(1)–Co(2)–Co(3)	60.0(1)	Co(1)–C(13)–Co(3)	78.0(7)
Ru(1)–Co(2)–C(6)	68.1(6)	Co(1)–C(13)–O(13)	143(2)
Co(1)–Co(2)–C(6)	121.5(6)	Co(3)–C(13)–O(13)	139(2)
Co(3)–Co(2)–C(6)	120.2(6)	Co(2)–C(23)–Co(3)	78.5(7)
Ru(1)–Co(2)–C(7)	168.6(6)	Co(2)–C(23)–O(23)	142(1)
Co(1)–Co(2)–C(7)	125.3(6)	Co(3)–C(23)–O(23)	140(1)

Experimental Section

General Procedures. Reactions and manipulations, except chromatographic separations, were carried out under N_2 using standard Schlenk tube techniques. Solvent were distilled before use. $HRuCo_3(CO)_{12}$,[1e] $HRuCo_3(CO)_{11}(PMe_2Ph)$,[10] $HRuCo_3(CO)_{11}(SMe_2)$,[11] $HRuCo_3(CO)_{11}(SeMe_2)$,[1c] $HRuCo_3(CO)_{11}(TeMe_2)$[3] were prepared by use of published procedures. SEt_2, $SeMe_2$, $TeMe_2$, $Me_3NO\cdot 2H_2O$, and PMe_2Ph were commercial samples and were used as received. Solution infrared spectra were recorded on a Nicolet 20SXC or a Bruker IFS-66 FT IR spectrometers. The UV–visible spectra were recorded on a Schimadzu UV-260 instrument. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer at 0 °C using $CDCl_3$ as the solvent. Chemical shifts are relative to TMS. ^{59}Co NMR spectra were measured on a Bruker MSL-300 instrument (71.21 MHz). The chemical shifts reported (ppm) for ^{59}Co are positive high frequency from

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Table 3. Selected Bond Distances (pm) and Angles (deg) for $HRuCo_3(CO)_9(PMe_2Ph)_3$ (3)

Bond Distances			
Ru–Co(1)	268.6(1)	Co(1)–H(1)	171(6)
Ru–Co(2)	270.0(1)	Co(2)–Co(3)	247.7(1)
Ru–Co(3)	266.6(1)	Co(2)–P(2)	221.8(2)
Ru–P(3)	235.2(2)	Co(2)–C(2)	193.0(8)
Ru–C(6)	188.2(9)	Co(2)–C(3)	199.1(7)
Ru–C(7)	187.7(8)	Co(2)–C(5)	175.7(8)
Ru–C(8)	247.9(9)	Co(2)–H(1)	172(6)
Co(1)–Co(2)	250.2(1)	Co(3)–C(1)	197.0(7)
Co(1)–Co(3)	247.8(1)	Co(3)–C(2)	198.6(8)
Co(1)–P(1)	219.5(2)	Co(3)–C(8)	177(1)
Co(1)–C(1)	193.8(7)	Co(3)–C(9)	175.7(9)
Co(1)–C(3)	195.0(7)	Co(3)–H(1)	170(6)
Co(1)–C(4)	175.5(8)		
Bond Angles			
Co(1)–Ru–Co(2)	55.36(3)	Co(1)–Co(2)–Co(3)	59.69(4)
Co(2)–Ru–Co(3)	55.15(3)	Co(1)–Co(2)–P(2)	117.75(7)
Co(3)–Ru–P(3)	110.51(6)	Co(1)–Co(2)–C(2)	111.2(2)
Co(1)–Ru–C(6)	153.3(2)	Co(1)–Co(2)–C(3)	49.9(2)
Co(1)–Ru–C(7)	96.3(3)	Co(1)–Co(2)–C(5)	131.7(2)
Co(2)–Ru–Co(3)	54.98(3)	Co(1)–Co(2)–H(1)	43(2)
Co(2)–Ru–P(3)	164.54(6)	Ru–Co(3)–Co(1)	62.84(3)
Co(2)–Ru–C(6)	99.2(2)	Ru–Co(3)–Co(2)	63.21(3)
Co(2)–Ru–C(7)	93.5(2)	Ru–Co(3)–C(8)	64.3(3)
Co(3)–Ru–P(3)	113.13(6)	Ru–Co(3)–C(9)	166.0(3)
Co(3)–Ru–C(6)	105.5(3)	Ru–Co(3)–H(1)	91(2)
Co(3)–Ru–C(7)	145.2(2)	Co(1)–Co(3)–Co(2)	60.66(4)
Ru–Co(1)–Co(3)	62.01(4)	Co(1)–Co(3)–C(1)	50.1(2)
Ru–Co(1)–P(1)	173.88(7)	Co(1)–Co(3)–C(2)	110.1(2)
Ru–Co(1)–C(4)	74.8(3)	Co(1)–Co(3)–C(8)	117.2(3)
Ru–Co(1)–H(1)	91(2)	Co(1)–Co(3)–C(9)	129.3(3)
Co(2)–Co(1)–Co(3)	59.65(4)	Co(1)–Co(3)–H(1)	44(2)
Co(2)–Co(1)–P(1)	123.35(7)	Co(1)–C(1)–O(1)	142.3(8)
Co(2)–Co(1)–C(1)	110.8(2)	Co(3)–C(1)–O(1)	138.9(8)
Co(2)–Co(1)–C(3)	51.3(2)	Co(2)–C(2)–O(2)	142.8(8)
Co(2)–Co(1)–C(4)	126.2(2)	Co(3)–C(2)–O(2)	138.6(9)
Co(2)–Co(1)–H(1)	43(2)	Co(1)–C(3)–O(3)	142.4(9)
Co(3)–Co(1)–P(1)	121.37(7)	Co(2)–C(3)–O(3)	138.7(8)
Co(3)–Co(1)–C(1)	51.2(2)	Co(1)–C(4)–O(4)	170.0(7)
Ru–Co(2)–Co(1)	62.04(3)	Co(2)–C(5)–O(5)	174.4(7)
Ru–Co(2)–Co(3)	61.81(3)	Ru–C(6)–O(6)	178.3(7)
Ru–Co(2)–P(2)	176.65(7)	Ru–C(7)–O(7)	179.3(7)
Ru–Co(2)–C(5)	85.4(3)	Co(3)–C(8)–O(8)	156.1(9)
Ru–Co(2)–H(1)	90(2)	Co(3)–C(9)–O(9)	177(1)

the external reference $K_3[Co(CN)_6]$ saturated in D_2O. Standard parameters are as follows: pulse width 3 ms; sweep width 263 kHz; number of scans between 5000 and 100000. Selected physical and spectroscopic data for the complexes are given in Table 1. When product stability allowed, elemental analyses are given. Reactions were monitored by IR spectroscopy or TLC.

Preparation of $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (2a,b). $HRuCo_3(CO)_{12}$ (0.200 g, 0.28 mmol) and PMe_2Ph (0.093 mL, 0.65 mmol) were refluxed for 1 h in CH_2Cl_2 (20 mL). The color of the solution changed from wine red to dark violet. According to ^1H NMR data, the relative amounts of **2a** and **2b** were not reproducible. Before chromatography, the following amounts were observed: 1 16%, **2a** 9% and **2b** 75%. Chromatographic separation using a hexane/CH_2Cl_2 5:1 mixture eluted some $HRuCo_3(CO)_{11}(PMe_2Ph)$ (1) (0.052 g, 0.058 mmol) followed by the violet title compound $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (**2b**) (0.095 g, 0.114 mmol, 66%). This reaction produced only traces of the trisubstituted cluster. The fraction of $HRuCo_3(CO)_{10}(PMe_2Ph)_2$, however, showed some tendency to form $HRuCo_3(CO)_9(PMe_2Ph)_3$ in solution. $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ was also prepared from $HRuCo_3(CO)_{11}(PMe_2Ph)$ plus PMe_2Ph (1:1 ratio) in CH_2Cl_2. After 1 h the products were separated by TLC and characterized by IR: only **2a** was found together with some unreacted **1**. Further addition of PMe_2Ph consumed all **1**, and **3** was produced. Traces of **2b** were observed after 2.5 h, and no **2a** was present after 24 h. Anal. Calcd for **2b**: $C_{26}H_{23}Co_3O_{10}P_2Ru$: C, 37.4; H, 2.78. Found: C, 37.0; H, 3.05. The ^1H-NMR signals of the hydride ligand are at δ −18.3 for the isomer **2b** with a Ru-bound phosphine and at δ −20.1 for the isomer **2a** with two axial, Co-bound phosphines.

Table 4. Crystallographic Data for $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (2b), and $HRuCo_3(CO)_9(PMe_2Ph)_3$ (3)

	2b	3
Formula	$RuCo_3C_{26}H_{23}O_{10}P_2$	$RuCo_3C_{33}H_{34}O_9P_3$
fw	835.28	945.39
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a(Å)	17.69(1)	10.927(5)
b(Å)	14.275(7)	21.275(5)
c(Å)	12.518(7)	16.096(3)
β (deg)	97.64(5)	94.65(3)
v(Å^3)	3133(3)	3729(1)
z	4	4
D_{calc}, g cm^{-3}	1.77	1.684
2Θ limits, deg	5–50	2–50
no. of unique reflcns	5505	7043
no. of obsd data	2280 ($I > 3\sigma(I)$)	3182 ($I > 2\sigma(I)$)
h, k, l range	−22, 22; 0, 17; 0, 15	0, 13; 0, 25; −19, 19
μ, mm^{-1} (λ = 0.709 26 Å)	2.12	1.87
no. params	379	542
R^a	0.0608	0.035
R_w^{b}	0.0567	0.031
GOF^c	1.4402	1.77
max residual, e Å^3; Δ/σ	1.68; 0.005	0.22; 1.31

$^a R = F - F_c/F_o$. $^b R_w = w(|F_o| - |F_c|)^2/w|F_o|^2]$. ^{c} GOF = $[w(|F_o| - |F_c|)^2/(NO - NV)]$; NO = number of observed reflections; NV = number of variables.

Preparation of $HRuCo_3(CO)_9(PMe_2Ph)_3$ (3). $HRuCo_3(CO)_{11}(PMe_2Ph)$ (1) (0.032 g, 0.044 mmol) and PMe_2Ph (0.014 mL, 0.098 mmol) were dissolved in CH_2Cl_2 (5 mL). The solution was stirred for 0.25 h at room temperature, the color changed from wine red to violet, Me_3NO (0.005 g, 0.045 mmol) was added, and the solution became immediately dark violet. After few minutes the TLC plates indicated the presence of only $HRuCo_3(CO)_9(PMe_2Ph)_3$. The solution was filtered, and the solvent was evaporated in vacuo. The resulting solid was extracted with toluene, and the toluene solution was evaporated to dryness, giving $HRuCo_3(CO)_9(PMe_2Ph)_3$ (**3**) as a black powder (0.028 g, 67%) UV(CH_2Cl_2): λ_{max} 326, 380(sh), 500, 600 (sh) nm. Anal. Calcd for $C_{33}H_{34}Co_3O_9P_3Ru$: C, 41.93; H, 3.63. Found: C, 42.6, H, 3.61.

The title compound was also obtained as a byproduct in the preparation of $HRuCo_3(CO)_{10}(PMe_2Ph)_2$. Prolonged reaction times led to evolution of the IR spectrum and appearence of new products by TLC. A violet solution was obtained after 24 h of reaction time, which showed IR absorptions at 2001 vs, 1942 s, 1801 s, 1788 (sh) cm^{-1} (in CH_2Cl_2). After 48 h of reaction time, the solution turned green and showed IR absorptions at 2002 m, 1954 vs, 1914 m, 1830 (sh), 1790 vs, 1766 vs cm^{-1}.

Reaction of $HRuCo_3(CO)_{11}(PMe_2Ph)$ with $TeMe_2$. $HRuCo_3(CO)_{11}(PMe_2Ph)$ (0.150 g, 0.21 mmol) and $TeMe_2$ (0.032 mL, ca. 0.21 mmol) were refluxed in CH_2Cl_2 (20 mL) for 25 h. Chromatographic separation produced unreacted $HRuCo_3(CO)_{11}(PMe_2Ph)$ (0.056 g, 0.08 mmol), $HRuCo_3(CO)_{10}(PMe_2Ph)(TeMe_2)$ (**4**) (0.059 g, 0.07 mmol, 33%), and finally a trisubstituted cluster (0.002 g), which was not fully characterized. Anal. Calcd for $C_{20}H_{18}Co_3O_{10}PRuTe$ (**4**): C, 28.1; H, 2.12. Found: C, 27.1; H, 2.73.

Reaction of $HRuCo_3(CO)_{11}(PMe_2Ph)$ with SEt_2. $HRuCo_3(CO)_{11}(PMe_2Ph)$ (1) (0.108 g, 0.15 mmol) and SEt_2 (0.016 ml, 0.15 mmol) were dissolved in hexane (30 mL), and solid Me_3NO (0.016 g, 0.15 mmol) was added. The wine red solution, which rapidly became deep red, was stirred for 0.25 h at room temperature. In the TLC separation with a hexane/toluene (1:1) mixture, two isomeric compounds were obtained. (i) $HRuCo_3(CO)_{10}(PMe_2Ph)(SEt_2)$ was obtained as the violet isomer (**5a**) (0.025 g, 21%). UV (CH_2Cl_2): λ_{max} 310, 379, 515, 600 (sh) nm. Anal. Calcd for $C_{22}H_{22}Co_3O_{10}PRuS$: C, 33.56; H, 2.82; S, 4.07. Found: C, 34.0; H, 3.0; S, 3.7; (ii) $HRuCo_3(CO)_{10}(PMe_2Ph)(SEt_2)$ was obtained as the brown isomer (**5b**) (0.046 g, 40%). UV(CH_2Cl_2): λ_{max} 311, 380, 475, 570 (sh) nm.

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (2b)

atom	*x*	*y*	*z*	U_{eq}[a]
Ru(1)	3169(1)	5155(1)	626(1)	37(1)
Co(1)	2372(1)	4666(2)	−1320(2)	36(1)
Co(2)	2024(1)	6161(1)	−457(2)	36(1)
Co(3)	1697(1)	4629(2)	308(2)	39(1)
P(2)	1702(3)	4374(3)	−2932(4)	50(2)
P(1)	3605(2)	5706(3)	2384(3)	39(1)
O(1)	3946(7)	3281(9)	1117(10)	70(5)
O(3)	4534(8)	5974(9)	−288(11)	77(6)
O(4)	3781(8)	3863(11)	−1818(13)	94(7)
O(6)	3043(8)	7539(8)	595(10)	68(5)
O(7)	1003(8)	7617(11)	−1412(11)	89(7)
O(8)	2295(7)	3946(9)	2404(11)	72(5)
O(9)	232(7)	3768(11)	474(13)	96(7)
O(12)	2931(7)	6397(9)	−2262(10)	66(5)
O(13)	2147(7)	2756(8)	−520(10)	70(5)
O(23)	1175(7)	6267(8)	1430(9)	59(5)
C(1)	3661(9)	3986(13)	934(13)	46(6)
C(3)	4031(10)	5665(13)	76(14)	55(7)
C(4)	3261(11)	4183(12)	−1603(16)	55(7)
C(6)	2729(10)	6890(13)	267(12)	48(7)
C(7)	1383(10)	7017(14)	−1076(15)	55(8)
C(8)	2213(10)	4289(13)	1597(17)	52(7)
C(9)	804(11)	4127(13)	367(15)	55(7)
C(12)	2612(10)	5948(12)	−1668(13)	49(7)
C(13)	2102(10)	3573(13)	−546(15)	53(7)
C(23)	1466(9)	5897(12)	771(13)	47(7)
C(201)	861(9)	5094(12)	−3289(13)	49(6)
C(202)	145(12)	4784(16)	−3052(17)	91(10)
C(203)	−494(12)	5337(21)	−3274(21)	109(13)
C(204)	−460(17)	6200(19)	−3684(20)	99(12)
C(205)	228(17)	6511(16)	−3906(22)	111(13)
C(206)	881(14)	5963(15)	−3711(18)	101(11)
C(211)	1366(13)	3203(13)	−3151(16)	92(10)
C(212)	2237(11)	4585(16)	−4072(13)	85(9)
C(101)	4144(9)	4840(11)	3222(12)	39(6)
C(102)	3854(11)	4332(13)	3983(13)	60(7)
C(103)	4248(15)	3647(18)	4598(18)	93(11)
C(104)	4979(17)	3475(14)	4420(17)	87(11)
C(105)	5322(12)	3980(14)	3677(17)	77(9)
C(106)	4891(11)	4663(13)	3095(14)	67(8)
C(111)	2902(9)	6146(13)	3168(13)	60(7)
C(112)	4271(10)	6709(11)	2460(13)	61(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for $HRuCo_3(CO)_9(PMe_2Ph)_3$ (3)

atom	*x*	*y*	*z*	U_{eq}[a]
Ru	2070.5(5)	2008.7(3)	7964.9(3)	36.1(3)
Co(1)	2389.9(8)	781.7(4)	7653.2(5)	32.3(5)
Co(2)	390.2(8)	1104.7(4)	8178.3(5)	33.7(5)
Co(3)	853.6(9)	1367.1(5)	6737.6(6)	40.6(6)
P(1)	7141(2)	197.8(9)	12609(1)	41(1)
P(2)	8970(2)	4630.3(9)	13276(1)	38(1)
P(3)	3709(2)	2602.2(9)	7515(1)	43(1)
O(1)	3098(5)	1014(3)	5955(3)	61(3)
O(2)	−1406(5)	1940(3)	7289(4)	70(4)
O(3)	2121(5)	472(3)	9414(3)	53(3)
O(4)	4849(4)	1154(3)	8230(3)	59(3)
O(5)	−262(5)	1795(3)	9622(3)	83(4)
O(6)	515(6)	3137(3)	8249(5)	100(5)
O(7)	3081(5)	1970(3)	9763(3)	67(4)
O(8)	1195(7)	2607(3)	6110(4)	104(4)
O(9)	−486(7)	991(5)	5192(4)	126(6)
C(1)	2465(6)	1028(3)	6499(4)	40(4)
C(2)	−550(7)	1621(4)	7374(5)	49(5)
C(3)	1820(6)	663(3)	8759(4)	34(3)
C(4)	3849(6)	1061(3)	8013(4)	42(4)
C(5)	49(6)	1539(4)	9059(5)	51(4)
C(6)	1101(7)	2722(4)	8133(5)	56(5)
C(7)	2707(6)	1985(4)	9084(4)	44(4)
C(8)	1198(8)	2159(4)	6508(5)	66(6)
C(9)	31(8)	1125(5)	5810(5)	68(6)
C(10)	4928(7)	2776(3)	8319(5)	45(4)
C(11)	6145(7)	2605(4)	8287(5)	59(5)
C(12)	7003(8)	2784(4)	8930(6)	76(6)
C(13)	6656(9)	3123(5)	9597(6)	82(6)
C(14)	5466(9)	3282(4)	9630(5)	77(6)
C(15)	4609(7)	3120(4)	9020(5)	62(5)
C(16)	6827(7)	717(3)	11718(5)	51(4)
C(17)	5884(8)	557(4)	11125(5)	62(5)
C(18)	5557(9)	932(4)	10457(5)	76(6)
C(19)	6162(9)	1462(5)	10347(6)	85(6)
C(20)	7110(9)	1643(4)	10879(6)	82(6)
C(21)	7445(8)	1274(4)	11591(6)	68(5)
C(22)	8140(6)	4817(3)	12278(4)	44(4)
C(23)	7232(8)	4418(4)	11944(5)	64(5)
C(24)	6671(9)	4528(5)	11169(5)	81(7)
C(25)	6957(9)	5017(6)	10709(5)	97(7)
C(26)	7823(9)	5425(5)	11032(6)	97(7)
C(27)	8421(7)	5326(4)	11813(6)	67(6)
C(28)	4507(8)	2301(4)	6665(5)	65(5)
C(29)	3306(8)	3378(4)	7138(6)	68(6)
C(30)	5734(7)	285(4)	13120(5)	64(5)
C(31)	8194(9)	604(5)	13321(6)	78(6)
C(32)	9490(8)	5386(4)	13714(5)	63(5)
C(33)	7756(7)	4431(4)	13942(5)	62(5)
H(1)	860(60)	710(30)	7330(40)	4.0[b]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Refined isotropically.

Reaction of $HRuCo_3(CO)_{11}(PMe_2Ph)$ with Me_3NO. Solid Me_3NO was added to a solution of $HRuCo_3(CO)_{11}(PMe_2Ph)$ (**1**) (0.050 g, 0.069 mmol) in CH_2Cl_2 (10 mL). Evolution of CO_2 occurred immediately, and the wine red solution became violet. After 0.25 h of stirring at room temperature, the solution was evaporated in vacuo. The resulting solid was extracted with a hexane/CH_2Cl_2 (80:20) mixture, and this solution was placed at −15 °C for 12 h, giving black crystals of $HRuCo_3(CO)_{10}(PMe_2Ph)(NMe_3)$ (**6a**) (0.035 g, 67%).

Reaction of $HRuCo_3(CO)_{10}(PMe_2Ph)(NMe_3)$ with SEt_2. $HRuCo_3(CO)_{10}(PMe_2Ph)(NMe_3)$ (**6a**) (0.030 g, 0.040 mmol) was dissolved in CH_2Cl_2 (5 mL) and SEt_2 (0.006 mL, 0.056 mmol) was added. The formation of a new violet compound was observed by TLC. After 0.5 h reaction at room temperature, the violet solution was evaporated in vacuo. The resulting solid residue contained only the violet isomer (**5a**) of $HRuCo_3(CO)_{10}(PMe_2Ph)(SEt_2)$ (0.025 g, 79%).

Reaction of $HRuCo_3(CO)_{11}(SMe_2)$ with PMe_2Ph. $HRuCo_3(CO)_{11}(SMe_2)$ (0.370 g, 0.57 mmol) was dissolved in CH_2Cl_2 (30 mL) and PMe_2Ph (0.081 mL, 0.57 mmol) was added. No change was observed by IR after 1 h reaction at room temperature. Chromatographic separation produced $HRuCo_3(CO)_{11}(PMe_2Ph)$ (**1**) (0.326 g, 0.45 mmol, 79%) and some $HRuCo_3(CO)_{10}(PMe_2Ph)_2$ (0.019 g, 0.02 mmol).

This reaction was also monitored by ^1H NMR at 20 °C where the resonances of $HRuCo_3(CO)_{11}(SMe_2)$ were observed at δ −19.6 ($Co_3(\mu_3\text{-}H)$) and at δ 2.15 (SMe_2). An equimolar amount of PMe_2Ph was then added to the NMR-probe. Collection of the first NMR-spectrum was completed ca. 5 min after the addition. This spectrum showed the signal of free SMe_2 (δ 2.1) and a minor signal of $HRuCo_3(CO)_{11}(SMe_2)$ (about 10%), although some PMe_2Ph was present according to the signals at δ 7.0–7.2 due to the PMe_2Ph phenyl protons. Accordingly, the $Co_3(\mu_3\text{-}H)$ hydride signal moved from δ −19.6 to δ −20.2 ($HRuCo_3(CO)_{11}(PMe_2Ph)$). After a reaction of $HRuCo_3(CO)_{11}(SMe_2)$ with PMe_2Ph (2:1 molar ratio) all the phosphine was consumed to form **1** and approximately equal intensity signals were observed for free and coordinated SMe_2.

Reaction of $HRuCo_3(CO)_{11}(SeMe_2)$ with PMe_2Ph. This reaction was monitored in a NMR tube at 0 °C where the resonances of $HRuCo_3(CO)_{11}(SeMe_2)$ (3.5 mol) were observed at δ −19.6 ($Co_3(\mu_3\text{-}H)$) and at δ 2.1 ppm ($SeMe_2$). An equimolar amount of PMe_2Ph was then added to the NMR-probe. The first NMR-spectrum was collected about 1 min after the addition. This spectrum showed the signals of free $SeMe_2$ (δ 2.0) and a very small signal at δ 2.1 due to the starting cluster. The $Co_3(\mu_3\text{-}H)$

hydride signal moved to δ −20.2 [corresponding to $HRuCo_3(CO)_{11}(PMe_2Ph)$] and also the phenyl protons showed only the two signals due to coordinated PMe_2Ph at δ 7.3 and δ 7.1. As in the SMe_2 reaction above some $HRuCo_3(CO)_{11}(SeMe_2)$ remained unreacted, even in the presence of a slight excess of phosphine.

Reaction of $HRuCo_3(CO)_{11}(TeMe_2)$ with PMe_2Ph. $HRuCo_3(CO)_{11}(TeMe_2)$ (0.145 g, 0.19 mmol) and PMe_2Ph (0.026 mL, 0.18 mmol) were stirred in a hexane/CH_2Cl_2 mixture for 20 min. Chromatographic separation produced $HRuCo_3(CO)_{11}(PMe_2Ph)$ (1) (0.030 g, 0.04 mmol) as a reddish brown band and $HRuCo_3(CO)_{10}(PMe_2Ph)(TeMe_2)$ (4) (0.096 g, 0.11 mmol, 58%) as a dark red band. Anal. Calcd for $C_{20}H_{18}Co_3O_{10}PRuTe$: C, 28.1; H, 2.12. Found: C, 28.2; H, 2.17.

X-ray Crystallography

Suitable black crystals of **2b** and **3** were obtained by slow crystallization from a CH_2Cl_2/hexane solution at −10 °C. Unit-cell parameters were calculated from the setting angles of 25 carefully centered high theta reflections. The intensities of three reflections were monitored every hour of exposure and showed no evidence of decay. Crystal data and intensity collection parameters are given in Table 4.

Structure Analysis and Refinement. Compound 2b. Diffraction measurements were carried out at room temperature on a Nicolet R3m diffractometer using graphite monochromatized Mo Kα radiation. The metal atom positions were solved by the direct methods of the SHELXTL Plus program package (SHELXTL Plus, Release 3.4, Nicolet Co., Madison, WI, 1988). All remaining non-hydrogen atoms were located by the usual combination of the full matrix least squares refinement and difference electron syntheses. The non-hydrogen atoms were refined anisotropically. Both the methyl and phenyl hydrogen atoms were placed in calculated positions (C–H = 0.96 Å; U = 0.08 Å^2) and not refined. An empirical absorption correction was made with SHELXTL. The positional parameters obtained from the last cycle of refinement are listed in Table 5, with the corresponding standard deviations.

Compound 3. Diffraction measurements were carried out at room temperature on a Enraf-Nonius CAD-4 four-circle diffractometer using graphite monochromatized Mo Kα radiation. After Lorentz and polarization corrections the structure was solved by direct methods which revealed the Ru, Co, and P atoms of the asymmetric unit.[12] The remaining non hydrogen atoms were located after successive scale factor refinements and Fourier difference methods. After isotropic (R = 0.057) refinement, an absorption correction was made with DIFABS.[13] After anisotropic refinement (R = 0.045), all the hydrogen atoms (in particular the hydridic H atom) were found using Fourier differences calculations. The whole structure was refined by full-matrix least-square methods (use of F magnitude; x, y, z, β_{ij} for Ru, Co, P, O and C atoms and x, y, z for H atoms; 542 variables and 3182 observations; $w = 1/\sigma(Fo)^2 = [\sigma^2(I) + (0.04\ Fo^2)^2]^{-1/2}$) with the residuals given in Table 4. Neutral atom scattering factors used for all atoms and anomalous dispersion coefficients were obtained from standard sources.[14] All the calculations were performed on a Digital MicroVax 3100 computer with the MOLEN package.[12] The positional parameters obtained from the last cycle of refinement are listed in Table 6, with the corresponding standard deviations.

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Supplementary Material Available: Atomic coordinates, including the hydrogen atoms (Tables S-I and S-IV), anisotropic thermal parameters (Tables S-II and S-V), and complete bond distances and angles (Tables S-III and S-VI) for complexes **2b** and **3**, respectively (16 pages). Ordering information is given on any current masthead page.

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