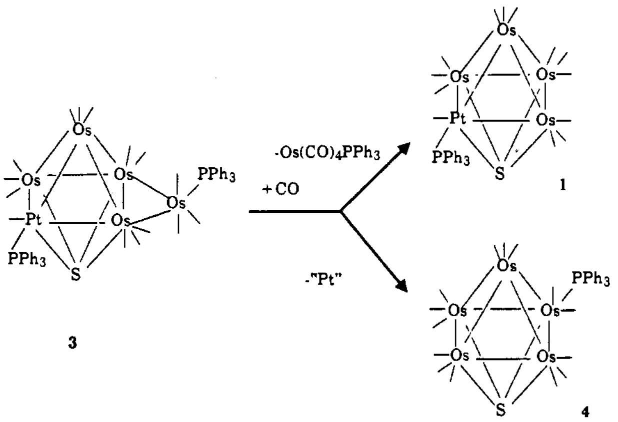
3 is similar to that of **1**, consisting of a square-pyramidal $PtOs_4$ group with the platinum atom in the square base and the square base bridged by a sulfido ligand.[13] However, **3** contains in addition an $Os(CO)_3PPh_3$ group bridging one of the osmium–osmium bonds in the base of the square pyramid. This group was clearly formed by the extrusion of one of the $Os(CO)_3$ groups from the cluster in **2**. It was stabilized in the bridging site by the addition of a PPh_3 ligand. This is supported by the observation that the yield of **3** is increased to 18% when the reaction is performed in the presence of 1 equiv of PPh_3. All the osmium atoms have three carbonyl ligands except Os(4), which has only two. The platinum atom contains one carbonyl ligand acquired presumably by migration from the osmium atoms. Although all details of the formation of **3** are not yet clear, the formation of platinum–sulfur bonding must be accompanied by a platinum insertion into an osmium–osmium bond.

It is easy to envisage the formation of **1** from **3** by the removal of the *edge*-bridging $Os(CO)_3PPh_3$ moiety. This was accomplished in 45% yield by treatment of **3** with CO. The formation of **1** was accompanied by formation of a corresponding amount of $Os(CO)_4PPh_3$. Surprisingly, this reaction also produced large amounts of **4**, indicating that the extrusion of the platinum moiety was also facile even though it had been incorporated into the main body of the cluster. The platinum-containing product from the latter reaction has not been identified. The existence of platinum–sulfur bonding in **3** provides further support for the notion that bridging ligands can play important roles in metal–metal-exchange reactions.[3,4]



Acknowledgment. This research was supported by the National Science Foundation under Grant No. CHE-8416460.

Supplementary Material Available: ORTEP drawings and tables of final fractional atomic coordinates, bond distances, and bond angles for both structural analyses (17 pages). Ordering information is given on any current masthead page.

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(12) Crystals of **3** were grown from CH_2Cl_2/hexane solutions under a CO atmosphere at −30 °C. The crystals belong to the triclinic space group $P\bar{1}$, No. 2, with $a = 12.538$ (2) Å, $b = 15.908$ (2) Å, $c = 18.061$ (2) Å, $\alpha = 63.008$ (9), $\beta = 76.629$ (9)°, $\gamma = 65.68$ (1)°, $Z = 2$, and $\rho_{calcd} = 2.414$ g/cm^3. The structure was solved by a combination of Patterson and difference Fourier techniques and was refined by using 4976 reflections ($F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals $R = 0.052$ and $R_w = 0.074$.

(13) Selected interatomic distances (Å) for **3** are Pt–Os(1) = 3.031 (1), Pt–Os(2) = 2.762 (1), Pt–Os(3) = 2.818 (1), Os(1)–Os(2) = 2.877 (1), Os(1)–Os(4) = 2.791 (1), Os(1)–Os(5) = 2.984(1), Os(2)–Os(3) = 2.896 (1), Os(2)–Os(4) = 2.823 (1), Os(3)–Os(4) = 2.719 (1), and Os(4)–Os(5) = 2.761 (1).

Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

Richard D. Adams*
James E. Babin
Rahina Mahtab
Suning Wang

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Mixed-Metal Gold Clusters. Synthesis and X-ray Structural Characterization of $[Au_5Re(H)_4(PPh_3)_7](PF_6)_2$ and $[Au_3Rh(H)(CO)(PPh_3)_5](PF_6)$

Sir:

There has been much recent interest in the synthesis and structural characterization of mixed transition metal gold clusters.[1-7] These compounds are important because of their potential use as bimetallic catalysts[8,9] and because of their intrinsically novel structures. The synthetic routes to these compounds have generally included (i) the combination of a carbonyl metalate with $AuPR_3X$, e.g. $[Os_4H_3(CO)_{12}]^- + AuClPPh_3 \rightarrow [Os_4H_3(CO)_{12}AuPPh_3]$,[11] and (ii) the replacement of metal hydrides by $AuPR_3$ units, e.g. $[(NO_3)Ir(PPh_3)_2H(AuPPh_3)_2]^+ + AuNO_3PPh_3 \rightarrow [(NO_3)Ir(PPh_3)_2(AuPPh_3)_3]^+$.[12] The structures of many of these clusters illustrate a close structural similarity between the hydride ligand and the $AuPR_3$ unit.[4,13]

It has become clear from the growing number of mixed-metal gold clusters that for many metals the transition metal to gold bond is thermodynamically favorable. In addition, bonds between gold atoms are favorable, as seen by the large number of stable gold phosphine clusters such as $[Au_9(PPh_3)_8]^{3+}$.[1,10] Gold clusters of this type have been synthesized by the reduction of $Au(PR_3)^+$ units; for example, the reaction of $AuNO_3PPh_3$ with $NaBH_4$ gives $[Au_9(PPh_3)_8](NO_3)_3$ in good yield.[10] Gold is partially reduced from +1 to $+^1/_3$ in this reaction. It therefore should be possible to synthesize large mixed-metal gold clusters by reaction of a coordinatively unsaturated mononuclear transition-metal hydride with a mononuclear gold(I) complex. In effect, the transition-metal hydride can reduce gold(I) and promote gold cluster growth. The coordinatively unsaturated transition-metal moiety that is produced by hydride loss or ligand dissociation can either trap a gold cluster fragment or participate directly in cluster growth, thereby forming a mixed-metal cluster. We have been successful with this conceptual approach and suggest that it is general for the synthesis of a large variety of mixed-metal gold clusters.

The reaction of 6 equiv of $AuNO_3PPh_3$ with a CH_2Cl_2 solution of $ReH_7(PPh_3)_2$[14] at −60 °C immediately gave a yellow solution. The addition of ethanol, removal of the CH_2Cl_2, and the addition of NH_4PF_6 yielded a precipitate. Yellow crystals of $[Au_5Re(H)_4(PPh_3)_7](PF_6)_2$ (**1**) were obtained in ca. 60% yield from a CH_2Cl_2–$(C_2H_5)_2O$ solvent mixture. The reaction of $RhH(CO)(PPh_3)_3$[15] with 1 equiv of $AuNO_3(PPh_3)$ in toluene solution at −78 °C yielded an orange-brown solid after gentle stirring for 12 h at 25 °C. A microcrystalline product was formed upon dissolving this solid in methanol and adding 2 equiv of KPF_6. Larger orange-brown crystals of $[Au_3Rh(H)(CO)(PPh_3)_5]PF_6$ (**2**) were obtained in 50% yield from a CH_2Cl_2–$(C_2H_5)_2O$ solvent mixture. All of the above manipulations were carried out under

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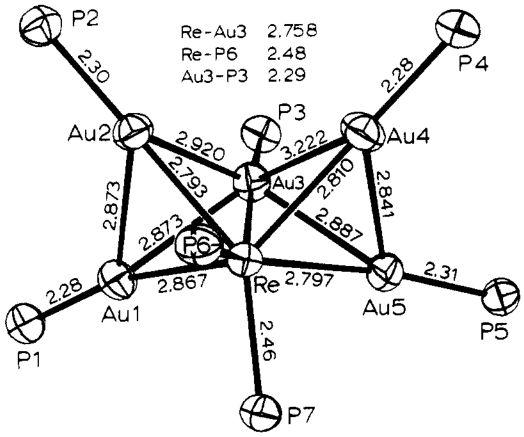

Figure 1. ORTEP drawing of the core of $[Au_5Re(H)_4(PPh_3)_7]^{2+}$ (in **1**). Selected distances (Å) and angles (deg) are as follows, where numbers refer to respective Au atoms. Distances: 2–4, 3.768; 1–5, 4.536. Angles: 1–Re–2, 61.00; 1–Re–3, 61.38; 1–Re–4, 129.45; 1–Re–5, 106.40; 2–Re–3, 63.46; 2–Re–4, 84.50; 2–Re–5, 122.73; 3–Re–4, 70.71; 3–Re–5, 62.60; 4–Re–5, 60.89; 1–3–5, 103.93; 2–3–4, 75.50; 1–3–2, 59.48; 4–3–5, 55.11; 3–1–2, 61.08; 3–2–1, 59.45; 3–5–4, 68.46; 3–4–5, 56.44; Re–1–P1, 167.0; Re–2–P2, 171.8; Re–3–P3; 175.0; Re–4–P4, 165.7; Re–5–P5, 170.1, P6–Re–P7, 93.5 (2). Esd in the last significant figure for all distances is 1, and those for angles involving only Au and Re and including P are 3 and 1, respectively.

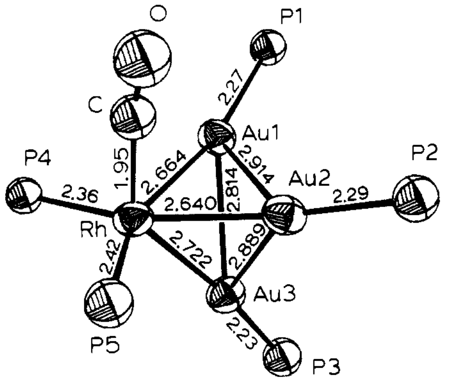

Figure 2. ORTEP drawing of the core of $[Au_3RhH(CO)(PPh_3)_5]^+$ (in **2**). Selected distances (Å) and angles (deg) are as follows, where numbers refer to respective Au atoms. Distance: C–O, 1.08 (6). Angles: 1–Rh–2, 66.65; 1–Rh–3, 62.99; 1–Rh–P4, 91.2; 1–Rh–P5, 155.3; 1–Rh–C, 77; 2–Rh–P4, 157.8; 2–Rh–P5, 88.6; 2–Rh–C, 80; 3–Rh–P4, 104.4; 3–Rh–P5, 108.5; 3–Rh–C, 135; 1–2–3, 58.02; 1–2–Rh, 57.08; 3–2–Rh, 58.78; 2–1–3, 60.55; 2–1–Rh, 56.27; 3–1–Rh, 59.51; 1–3–2, 61.43; 1–3–Rh, 57.50; 2–3–Rh, 56.03; Rh–1–P1, 165.2; Rh–2–P2, 170.9; Rh–3–P3, 172.2; P4–Rh–P5, 113.6; P4–Rh–C, 97; P5–Rh–C, 98; Rh–C–O, 170 (6). Esd's in last significant figure for distances Au–Au, Rh–Au, M–P, and Rh–C are 2, 3, 1, and 6, respectively, and for angles M–M–M, M–M–P, M–M–C, P–Rh–P, and P–Rh–C are 8, 3, 2, 3 and 2, respectively.

an N_2 atmosphere with standard Schlenk techniques.

Crystals of **1** and **2** were subjected to single-crystal X-ray analysis.[16] The structures of the coordination cores of both compounds with selected distances and angles are shown in Figures 1 and 2. The structure of **1** consists of a significantly distorted edge-shared bi-tetrahedron. A similar but less distorted geometry was found in $[Au_6(PPh_3)_6]^{2+}$.[17] The primary distortion is the elongation of the nonbonded Au1–Au5 distance (4.536 (1) Å) and the shortening of the Au2–Au4 (3.768 (1) Å). This is a distortion toward the bicapped tetrahedron geometry. The Au–Au bonded distances (average 2.936 (1) Å) show significant variation, as is common in gold clusters, and this is due to the soft nature of the bonding. The Au–P vectors are all nearly trans to the Re atom (average P–Au–Re = 169.9 (1)°), as is typical in iridium-gold phosphine clusters.[2] The average Re–Au and Re–P distances are 2.805 (1) and 2.47 (1) Å, respectively. The Re–P distances are long compared with those in $ReH_7(PPh_3)_2$ (2.427 (1) Å),[14] and this probably results from the higher coordination number in **1**. The tetrahyrido formulation for **1** (vide infra) indicates a formal coordination number of 11 for Re. Consistent with this, the P–Re–P angle (93.5 (2)°) in **1** is small compared with 134° in ten-coordinate $\{Ag[ReH_7(PPh\text{-}i\text{-}Pr_2)_2]_2\}^+$[18] and 138.9° in nine-coordinate $ReH_7(PPh_3)_2$.[14] The structure of **2** consists of a Au_3Rh tetrahedron. The Rh atom is seven-coordinate including the hydride, which is most reasonably positioned trans to the carbonyl group (vide infra). The Rh–P and Rh–C distances (average 2.39 (1) and 1.95 (6) Å) are long compared with the averages 2.32 and 1.83 Å, respectively, in $RhH(CO)(PPh_3)_3$,[19] and this reflects the higher coordination number in **2**. The Au–P vectors are approximately trans to the Rh atom (average P–Au–Rh = 169.4 (3)°) as observed in **1**. The average Au–Au and Au–P distances (2.872 (2) and 2.26 (1) Å, respectively) are similar to those in **1**, and the average Rh–Au distance (2.675 (3) Å) is similar to the average Ir–Au distance in $[Au_4Ir(H)_2(PPh_3)_6]^+$.[2] The positions of the hydride ligands in **1** and **2** were not located in the X-ray analyses. These compounds are the first well-characterized examples of Re and Rh gold clusters.

Solution NMR spectroscopic data of **1** and **2** are entirely consistent with their solid-state structures and are important in determining the hydride formulations. The $^{31}P\{^1H\}$ NMR spec-

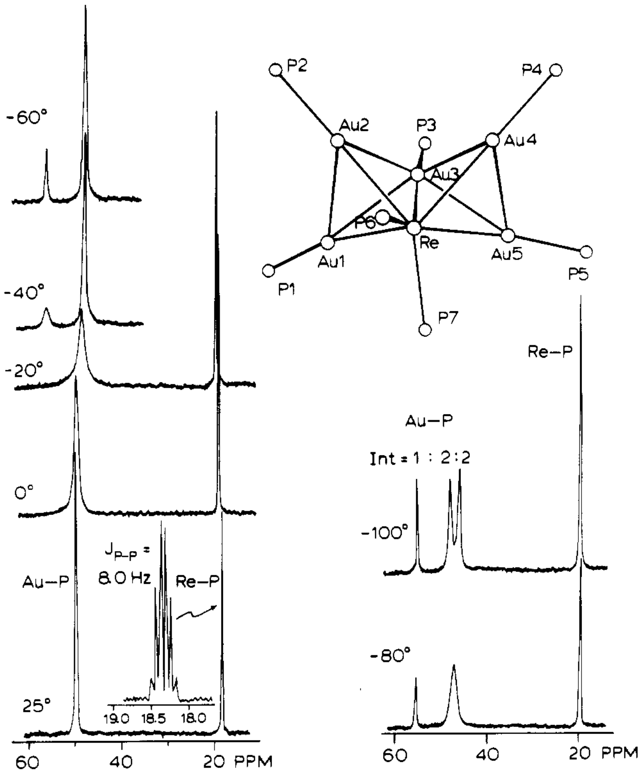

Figure 3. $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz) of **1** recorded at several temperatures with use of CH_2Cl_2 as solvent. Shifts are relative to internal standard trimethyl phosphate with positive shifts downfield.

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(16) Details of experimental procedures are included as supplementary material and are the same as published in ref 2. Both crystals were unstable upon removal from the solvent and therefore were sealed in capillary tubes that contained some solvent. Compound **1** crystallized as a diether solvate in the space group $P\bar{1}$: $a = 17.198$ (2) Å, $b = 19.061$ (7) Å, c 22.181 (8) Å, $\alpha = 88.04$ (2)°, $\beta = 78.62$ (2)°, $\gamma = 69.49$ (2)°, $V = 6672$ (4) Å^3, $Z = 2$, $\rho_c = 1.716$ g cm^{-3}; 7762 independent observed reflections [$2\theta_{max} = 42°$, $F_o^2 \geq 3\sigma(F_o^2)$], $R = 0.045$. Compound **2** crystallized as an ether solvate in the orthorhombic space group $Pna2_1$ (No. 33): $a =$ 44.131 (7) Å, $b = 15.418$ (2) Å, $c = 12.940$ (6) Å, $V = 8805$ Å^3, $Z = 4$, $\rho_c = 1.723$ g cm^{-3}; 2718 independent observed reflections [$2\theta_{max} = 44°$, $F_o^2 \geq 1\sigma(F_o^2)$], $R = 0.060$.

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trum of **1** recorded at several temperatures is shown in Figure 3. At 25 °C the Au–P groups are equivalent (broad single resonance δ 49.7) due to a rapid skeletal rearrangement, but at −100 °C the Au–P resonance has split into three peaks in a 1:2:2 ratio. This pattern is consistent with the edge-shared bi-tetrahedral structure. The dynamic rearrangement is not due to rapid phosphine or $AuPPh_3$ dissociation because P–P and P–H coupling is observed in the 25 °C spectrum. The ^1H NMR spectrum (CD_2Cl_2, 25 °C, 300 MHz) of **1** shows an eight-line multiplet in the hydride region at δ −2.07. Selective phosphorus decoupling gave a sextet [$J(H-P_{Au})$ = 9.1 Hz] with Re–P decoupled and a triplet [$J(H-P_{Re}]$ = 18.6 Hz] with Au–P decoupled. Careful integration of this hydride resonance vs. the aromatic region and vs. the para-CH_3 peak in the *p*-tolylphosphine PAr_3 derivative $[ReH_4(PAr_3)_2(AuPPh_3)_5]^{2+}$ consistently gave 4.0 ± 0.1 hydrides.[20] The positions of the hydrido ligands could not be deduced from the available data. It is likely that hydride bridging between Re and Au occurs due to the crowded nature of the Re core; however, the nonrigid nature of the complex in solution makes this difficult to prove.

The $^{31}P\{^1H\}$ NMR spectrum (reference trimethyl phosphate, CH_2Cl_2, 25 °C, 121.5 MHz) of **2** showed a doublet of quartets resonance at δ 58.6 [J(P–Rh) = 125 Hz, J(P–P) = 41 Hz, integration = 2] assigned to RhP and a triplet of doublets resonance at δ 41.9 [J(P–P) = 41 Hz, J(P–Rh) = 14 Hz, integration 3] assigned to AuP. The compound is nonrigid since in the solid state P3 is nonequivalent to P1 and P2. The ^1H NMR spectrum (CD_2Cl_2, 25 °C, 300 MHz) shows a multiplet at δ −4.91 with integration of 1.0 ± 0.1 H (integration vs. phenyl hydrogens). The multiplet spectrum was successfully computer-simulated with use of the above coupling constants and J(Rh–H) = 8.4, $J(H-P_{Rh})$ = 6.5, and $J(H-P_{Au})$ = 13.0 Hz.[21] The placement of the hydride trans to the CO group is likely on the basis of the solid-state structure. This position is exactly correct for bridging to Au3. The hydride could of course be bent away from Au3, but the observation that the Rh–Au3 distance is significantly longer than the other Rh–Au bonds supports a bridging formulation. The infrared spectra (solution and KBr disk) of **1** and **2** show no evidence for terminal metal–hydride stretches in the 1800–2200-cm^{-1} region. The bridging region is complex due to other absorptions, and thus for M(μ-H)Au bands have not been identified.

The formation of **1** and **2** in high yield supports the synthetic approach discussed above for mixed-metal gold clusters. Both of the starting transition-metal hydride compounds are known to easily become coordinatively unsaturated. $RhH(CO)(PPh_3)_3$ shows extensive phosphine dissociation at room temperature in benzene solution,[15] and $ReH_7(PPh_3)_2$ undergoes thermal as well as photochemical elimination of H_2 to produce the 16-electron species $ReH_5(PPh_3)_2$.[22] These complexes should also be capable of reducing gold(I). Gold is reduced in the formation of **1** and **2** from $AuNO_3PPh_3$. This general synthetic approach is currently being successfully used in the synthesis of other mixed-metal gold clusters.

Acknowledgment. This work has been supported by the National Science Foundation (NSF Grant CHE-81-08490) and by the University of Minnesota Graduate School.

Supplementary Material Available: Experimental details of the X-ray structure determination, tables of crystal structure data collection and refinement parameters (Table 1), final atom positional and thermal parameters (Tables 2 and 3), and weighted least-squares planes (Tables 4 and 5), figures of ORTEP drawings of the molecular structures (Figures S1 and S2) and ^1H and ^{31}P NMR spectra for **1** and **2** (Figures S3–S5) (28 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455

Paul D. Boyle
Brian J. Johnson
Angela Buehler
Louis H. Pignolet*

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[20] Integrations were done on several different samples and with use of a variety of instrument conditions. The results always gave 4 hydride ligands. Our experience with many different polyhydrido clusters gives us confidence in this NMR result. Conductivity measurements on **1** as the *p*-tolyl derivative also confirmed the dicationic formulation so the possible alternate diamagnetic hydride possibilities are 2 or 6. It is unlikely that the NMR integrations are wrong by this amount.

[21] NMR simulation was done with the Nicolet program NMCSIM and is described in the Nicolet Magnetics Corp. 1280 program manual. The spectrum is included as supplementary material.

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Unusual Route to an Acyl Complex in Cluster Chemistry: Synthesis, Structure, and Reactivity of $Ru_3(\mu\text{-}\eta^2\text{-}C(O)(C_6H_5))(\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$

Sir:

Recent discoveries[1,2] of catalytic systems for substitution of CO by phosphine ligands in $Ru_3(CO)_{12}$ have opened the field to studies of monosubstituted cluster complexes that could not be accessed through thermal routes.[3]

Typically, thermal reaction of diphenylpyridylphosphine (PPh_2py) with $Ru_3(CO)_{12}$ was previously shown to give $Ru_3(CO)_9(PPh_2py)_3$, as well as monomeric species.[4] A reinvestigation of this reaction using either sodium benzophenone ketyl[1] or [PPN]CN[2] led us to prepare $Ru_3(CO)_{11}(PPh_2py)$ (**1**) selectively and quantitatively.[5] Notably, the catalysts did not promote subsequent coordination of the nitrogen atom, since the expected complex $Ru_3(CO)_{10}(\mu\text{-}\eta^2\text{-}PPh_2py)$ was not observed. By contrast, **1** is observed to be metastable at ambient temperature, yielding the new cluster complex $Ru_3(\mu\text{-}\eta^2\text{-}C(O)(C_6H_5))(\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**2**),[6] which is fully characterized by IR, ^{31}P and ^{13}C NMR,[6] and X-ray diffraction[7] methods.

As shown in Figure 1, the structure of this 50-e cluster involves an open trinuclear ruthenium framework. Oxidative cleavage of a phosphorus–carbon bond in diphenylpyridylphosphine has provided the organic fragment $P(C_6H_5)(C_5H_4N)$, which is capping one face of the metal triangle through the bridging phosphido group, which spans the open Ru(2)···Ru(3) edge and is also coordinated to Ru(1) through the nitrogen atom.

A further feature of interest in the structure consists of a bridging acyl group $-O{=}C(C_6H_5)$ across Ru(2)···Ru(3).

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[5] Both methods afforded the red complex $Ru_3(CO)_{11}P(C_6H_5)_2(C_5H_4N)$ (**1**) in 100% spectroscopic yield within 2 min. IR (νCO, cm^{-1}; cyclohexane): 2093 (w), 2041 (m), 2025 (s), 1992 (w). This spectrum could be unambiguously assigned to the monosubstituted complex by comparison with related spectra of a variety of substituted complexes (see for example ref 1a). The complex could not be chromatographed, since its conversion into **2** (see ref 6) was accelerated on the column at 25 °C.

[6] The slow conversion of **1** into **2** is observable in solution at 25 °C. The reaction is complete within 2 h in THF at 40 °C. Chromatographic workup on silica gel (CH_2Cl_2/petroleum ether as eluent) affords the yellow complex $Ru_3(\mu\text{-}\eta^2\text{-}C(O)(C_6H_5))(\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**2**) as the only detectable product (yield 85%, recrystallized). Anal. Calcd for $C_{27}H_{14}NO_{10}PRu_3$: C, 38.31; H, 1.65; N, 1.65. Found: C, 37.09; H, 1.65; N, 1.58. IR (νCO, cm^{-1}; hexane): 2060 (w), 2045 (vs), 2020 (s), 1992 (m), 1973 (m), 1955 (w). ^{13}C NMR (−60 °C; CD_2Cl_2): δ 302.37 (d, acyl carbon). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.93.

[7] (a) Crystal data for compound **2**: orthorhombic, space group $P2_12_12_1$, a = 10.431 (2) Å, b = 15.888 (5) Å, c = 17.821 (5) Å, V = 2953.44 Å^3, Z = 4. Data in the range $2 < 2\theta(\text{Mo K}\alpha) < 55°$ were collected on an Enraf-Nonius CAD4 diffractometer. Data collection, reduction, and refinement procedures were similar to those detailed in a previous publication.[7b] Full-matrix least-squares refinements of 379 variables for 2757 reflections with $F_o^2 > 3\sigma(F_o^2)$ led to R = 0.043 and R_w = 0.049. (b) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Organometallics* **1982**, *1*, 1040.

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