$w = 1.53/(\sigma^2(F) + 0.002F^2)$. Refinement converged to the residuals $R = 0.069$ and $R_w = 0.072$.

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Supplementary Material Available: For **2c**, lists of bond lengths and angles, least-squares planes, and atomic fractional coordinates and thermal parameters (4 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Study of the Reactivity of the Nitriles RCN (R = CH_3, C_6H_5) toward the Unsaturated $(PPh_3)_2(CO)HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ Complex: Reversible Hydrogen Elimination (R = Me) or Hydrometalation Reactions (R = C_6H_5)

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The complex $(PPh_3)_2(CO)HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (**1**) reacts with acetonitrile to give $(PPh_3)_2(CO)Re(\mu\text{-}H)_3Ru(MeCN)(PPh_3)_2$ (**2**). The reaction is reversible under hydrogen at atmospheric pressure. The complex **1** reacts with benzonitrile to afford $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$ (**3**), which results from a hydrometalation of the nitrile. Complex **3** has been both spectroscopically and crystallographically characterized. Crystallographic data for **3**: monoclinic, $P2_1/n$, $a = 14.775$ (2) Å, $b = 23.775$ (2) Å, $c = 21.695$ (3) Å, $\beta = 92.53$ (1)°, $V = 7613$ (2) Å^3, $Z = 4$, $R = 0.049$, $R_w = 0.060$ for 4489 observations ($F_o^2 > 3\sigma(F_o^2)$) and 299 variable parameters. Under CO at atmospheric pressure, the benzonitrile ligand in **3** is easily displaced to give $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(CO)(PPh_3)_2)$ (**4**). Under 10 atm of hydrogen, **3** reverts to **1** with liberation of benzonitrile and formation of traces of benzylamine.

Introduction

We have recently shown that $ReRuH_5(CO)(PPh_3)_4$ (**1**), an unsaturated heterodinuclear complex resulting from the reaction of $[ReH_6(PPh_3)_2]^-$ with $RuHCl(CO)(PPh_3)_3$, was readily protonated, leading to the first example of a heterodinuclear complex containing molecular hydrogen, $[ReRu(H_2)H_4(CO)(PPh_3)_4]^+$.[1]

Pursuing the study of the reactivity of complex **1**, we have investigated possible reactions with nitriles.

Indeed, homogeneous hydrogenation of heteroatomic triple bonds is not usually an easy process.[2] The literature gives examples of hydrometalation of nitriles either with an unsaturated dimetallic rhenium hydride complex[3] or with $Ru_3(CO)_{12}$ under a hydrogen atmosphere.[4] Therefore, it was tempting to test the reactivity of our mixed Re–Ru unsaturated complex **1** toward nitriles, RCN. In this paper, we report two types of reactions which have been actually observed: (i) a reversible substitution reaction of two hydride ligands by the incoming nitrile (R = CH_3); (ii) a substitution reaction *and* a hydrometalation of the nitrile leading to a complex containing a benzonitrile ligand and a benzylideneimido ligand (R = C_6H_5).

Results and Discussion

Reactivity of $ReRuH_4(CO)(PPh_3)_4$ (1) toward Acetonitrile. The complex **1** dissolves in acetonitrile at room temperature, and the brown precipitate **2** rapidly appears (Scheme I). The infrared spectrum (Table I) of **2** shows that the ν_{CO} stretching wavenumber is lowered by 65 cm^{-1} compared to that for **1** and an absorption is observed at 2255 cm^{-1}, which can be attributed to the ν_{CN} stretching vibration of a coordinated acetonitrile. The ^1H NMR spectrum confirms the presence of coordinated acetonitrile, as a resonance is observed at 1.21 ppm, which is integrated as three protons by comparison with the phenyl resonances. In the hydride region, at 298 K, three resonances in a 1/1/1 intensity ratio are observed: two broad ones centered at −4.42 and −5.64 ppm, and a third one, an unresolved multiplet, at −14.38 ppm. At 193 K, the last signal remains the same but the broad resonances become a doublet and a double pseudotriplet centered at −3.39 and −6.15 ppm, respectively. The room-temperature $^{31}P\{^1H\}$ NMR spectrum shows two broad signals of equal intensities centered at 60.2 and 42.5 ppm. At 193 K, these two signals split into four resonances of equal intensity: one doublet centered at 73.6 ppm, a doublet of doublets centered at 58.2 ppm, one doublet centered at 45.65 ppm, and a singlet at 42.5 ppm. By analogy with the $^{31}P\{^1H\}$ NMR data for **1**,[1] we attribute the two signals observed at low field to the phosphine ligands bonded to ruthenium. Se-

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Table I. Spectroscopic Data for the Isolated Complexes

	IR, cm^{-1} [a]				
	ν_{CN}	ν_{CO}	^{1}H NMR, δ [b]	^{31}P NMR, δ [b]	*T*, K
2	2255	1800	1.21 (s, CH_3CN); −4.42 (br); −5.64 (br); −14.38	60.2; 42.5	293
			1.25 (CH_3CN); −3.39 (d, H_A, $J_{P_AH_A}$ = 64.9); −6.15 (ddd, H_B, $J_{P_BH_B}$ = 61.3, $J_{P_CH_B}$ = 20, $J_{P_AH_B}$ = 13); −14.39 (unresolved multiplet, H_C)	73.6 (d, P_A, $J_{P_AP_B}$ = 20.5); 58.2 (dd, P_B, $J_{P_BP_C}$ = 20.8); 45.6 (d, P_C); 42.5 (s, P_D)	193
3	2211	1795	8.21 (d, N=CHPh, J_{PCH} = 7.3); −8.45 (dd, H_A, $J_{P_AH_A}$ = 68.9, $J_{P_BH_A}$ = 12.6); −9.03 (ddt, H_B, $J_{P_AH_B}$ = 15.4, $J_{P_BH_B}$ = 61.5, $J_{P_CH_B}$ = $J_{P_DH_B}$ = 13.9)	53.3 (d, P_A, $J_{P_AP_B}$ = 21.6); 42.8 (dd, P_B, $J_{P_BP_D}$ = 19.4); 33.9 (s, P_C); 30.1 (d, P_D)	293
4		1946, 1798	9.06 (d, N=CHPh, J_{PCH} = 8.5); −8.77 (ddd, H_A, $J_{P_BH_A}$ = 58, $J_{H_AH_B}$ = 7, $J_{P_AH_A}$ = 13); −9.14 (H_B, $J_{P_AH_B}$ = 71, $J_{P_BH_B}$ = 13, $J_{H_AH_B}$ = 7)	45.1 (d, P_A, $J_{P_AP_B}$ = 20.1); 38.8 (dd, P_B, $J_{P_BP_D}$ = 20.4); 31.6 (s, P_C), 30.7 (d, P_D)	

[a] CH_2Cl_2 solutions. [b] δ in ppm, *J* in Hz.

lective phosphorus decoupling experiments performed at 193 K allowed us to attribute all the phosphorus–hydride coupling constants (Table I). All these spectroscopic data as well as the chemical analysis are consistent with the $ReRuH_3(CO)(PPh_3)_4(CH_3CN)$ formulation for **2**.

The ^{13}C NMR spectrum of the crude compound confirms that there is no signal which can be attributed to a hydrometalated acetonitrile ligand. Moreover, even in boiling acetonitrile, only **2** is formed, without any evidence of other product. So, we can conclude that the reaction of acetonitrile with **1** only leads to a hydrogen displacement without hydride migration onto the nitrile ligand. It has to be pointed out that this reaction is easily reversible, since bubbling hydrogen into a solution of **2** in dichloromethane rapidly regenerates **1**.

Due to the failure in obtaining suitable single crystals for an X-ray diffraction study, the proposed structure for **2** will be presented after the discussion of the structure of the product resulting from the reaction of **1** with benzonitrile (vide infra).

Reactivity of $ReRuH_5(CO)(PPh_3)_4$ (1) toward Benzonitrile. **1** reacts slowly with benzonitrile at room temperature, leading to the new product **3** (Scheme I), which can be isolated by crystallization from a dichloromethane/hexane mixture. The IR spectrum of **3** is very similar to that of **2**: it presents a ν_{CO} absorption at 1795 cm^{-1} and a ν_{CN} absorption at 2211 cm^{-1}. Nevertheless, NMR data give strong evidence that **3** had a formulation different from that of **2**. The ^{1}H NMR spectrum (Table I) shows that the molecule contains only two hydride ligands which are not fluxional on the NMR time scale. A doublet centered at 8.21 ppm (J_{PH} = 7.3 Hz) is also observed, which suggests that hydrometalation of benzonitrile has occurred. This is corroborated by the ^{13}C NMR spectrum of **3**, which shows the presence of a CH group centered at 168.5 ppm (J_{CH} = 166 Hz), consistent with the formation of a N=CHPh ligand. The ^{13}C NMR spectrum also shows the presence of a PhCN ligand, the CN resonance being observed at 126.1 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows four different resonances for the phosphine ligands (Table I). All these data and the chemical analysis are in agreement with the $ReRuH_2(CO)(PPh_3)_4(PhCN)(PhHCN)$ formulation. Single crystals of **3** were grown from an acetone solution, and an X-ray diffraction analysis has been performed.

A perspective view of complex **3** is given in Figure 1, along the labeling scheme. Bond lengths and bond angles of interest are gathered in Table II. The structure of complex **3** consists, in accordance with spectroscopic data, of a dinuclear ReRu unit in which the two metal centers are symmetrically bridged by a benzylideneimido ligand and two bridging hydrides, which have been located directly in the X-ray study. The coordination spheres of the metal atoms are completed by two phosphines and one terminal carbonyl ligand for the Re atom and by two phosphines and one benzonitrile ligand for the Ru atom. The overall structure can be described as two distorted octahedra sharing the H(1)H(2)N(2) face, the P(1) phos-

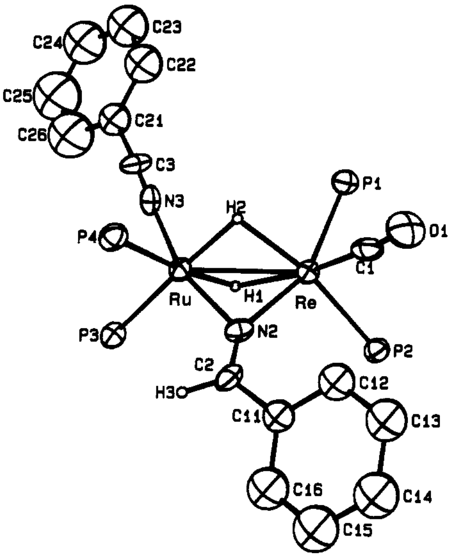
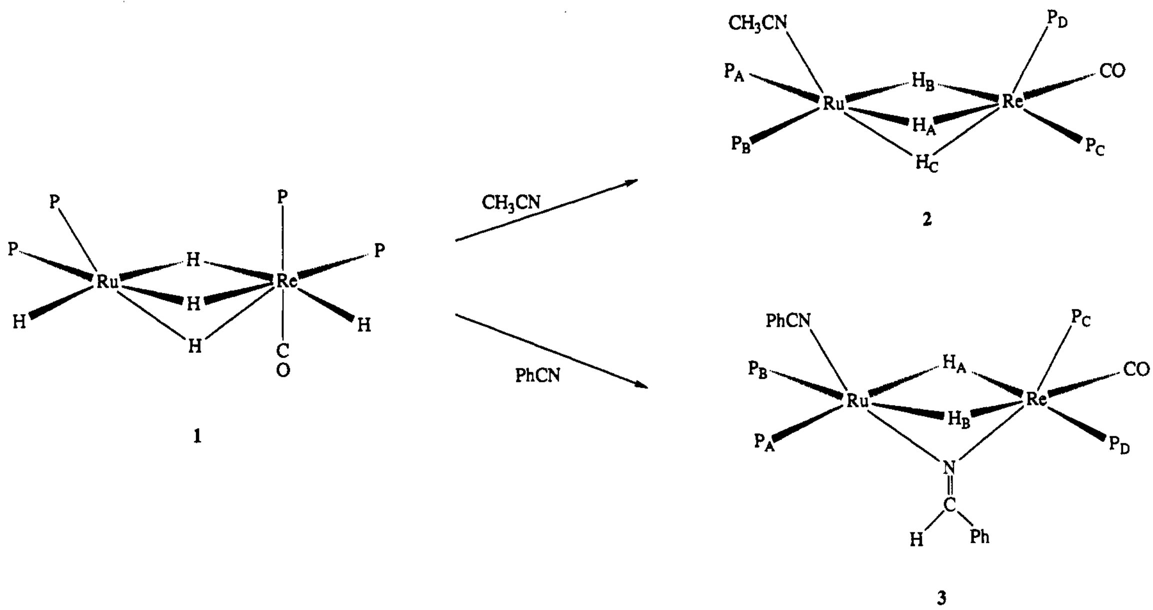


Figure 1. Perspective view of the complex $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$ (**3**). Vibrational ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms, which have been put on an arbitrary scale. For clarity phenyl rings attached to P(1), P(2), P(3), and P(4) have been omitted.

Table II. Bond Lengths (Å) and Angles (deg) of Interest for Compound 3

Re–Ru	2.654 (1)	Ru–N(2)	2.03 (1)
Re–N(2)	2.08 (1)	Ru–H(1)	1.6 (1)
Re–H(1)	1.8 (1)	Ru–H(2)	1.6 (1)
Re–H(2)	1.9 (1)	Ru–N(3)	2.03 (1)
Re–C(1)	1.82 (2)	Ru–P(3)	2.330 (4)
Re–P(1)	2.348 (4)	Ru–P(4)	2.354 (4)
Re–P(2)	2.345 (4)	N(2)–C(2)	1.27 (2)
C(3)–C(21)	1.41 (2)	C(2)–C(11)	1.47 (2)
		N(3)–C(3)	1.16 (2)
C(1)–Re–N(2)	103.5 (6)	C(1)–Re–P(2)	90.1 (4)
C(1)–Re–Ru	85.1 (5)	N(3)–Ru–N(2)	162.6 (5)
N(3)–Ru–P(3)	86.1 (4)	N(3)–Ru–P(4)	95.3 (4)
N(2)–Re–P(2)	100.4 (3)	N(2)–Ru–P(3)	105.9 (3)
N(2)–Re–P(1)	156.1 (3)	N(2)–Ru–P(4)	94.2 (4)
P(2)–Re–P(1)	101.8 (1)	P(3)–Ru–P(4)	102.2 (2)
Ru–N(2)–Re	80.6 (4)	C(2)–N(2)–Re	146 (1)
N(2)–C(2)–C(11)	129 (1)	C(2)–N(2)–Ru	134 (1)
N(3)–C(3)–C(21)	176 (2)	N(2)–C(2)–C(11)	129 (1)
H(1)–Re–P(1)	96 (4)	H(1)–Ru–P(3)	93 (4)
H(1)–Re–P(2)	103 (4)	H(1)–Ru–P(4)	163 (4)
H(2)–Re–P(1)	87 (4)	H(2)–Ru–P(3)	173 (4)
H(2)–Re–P(2)	167 (4)	H(2)–Ru–P(4)	84 (4)

Scheme I



phine, and the benzonitrile ligands being in a position trans to N(2).

The rhenium–phosphorus distances are equal within the experimental errors and are not sensitive to the nature of the trans ligands (e.g. Re–P(1)(trans to N(2)) = 2.348 (4) Å and Re–P(2)(trans to H(2)) = 2.345 (4) Å). The carbon–nitrogen bond length in the benzonitrile ligand coordinated to the ruthenium atom (C(3)–N(3) = 1.16 (2) Å) is not significantly different from the C≡N bond length found in free benzonitrile (1.137 (14) Å),[5] and the arrangement of the C(21)–C(3)–N(3) atoms is linear (∠N(3)–C(3)–C(21) = 176 (2)°). These observations are in contrast with those made for a copper complex containing benzonitrile, CuCl·PhCN, in which a shortening of the C–N bond was observed.[6] For the benzylideneimido ligand, the metal–nitrogen bond lengths are not significantly different from the ones found for alkylideneimido ligands in a similar situation.[3,4,7] The phenyl group is positioned anti to the Ru atom.

An electron count indicates that **3** is a 32-valence-electron complex, but this unsaturation is not reflected by the Re–Ru bond distance (Re–Ru = 2.654 (1) Å), which is in the area of the sum of covalent bond radii of the two metals.[8]

Having now a precise knowledge of the structure of **3**, we may tentatively assign the signals observed in the ^1H and ^{31}P NMR spectra (Table I). First, the proton attached to the carbon of the benzylideneimido ligand is coupled to the P_C nucleus, and this allows us to attribute the P_C resonance to the P(1) atom, which is in a transoid position with H(3). Since the H_B resonance shows equal coupling to the two phosphorus nuclei bonded to rhenium, it seems reasonable to attribute this signal to H(1). As a consequence, the P_B resonance is attributed to the P(4) atom, and the H_A and P_A resonances are assigned to the H(2) and P(3) atoms, respectively.

The structure of **3**, as has been established by the X-ray diffraction study, gives evidence that the structure we have proposed for **1** is incorrect.[1] Indeed, the lowering of the ν_{CO} frequency from 1930 cm^{-1} for $RuHClCO(PPh_3)_3$ to 1865 cm^{-1} in **1** suggested that the carbonyl ligand was in a bridging position. In fact, if now we compared the IR data for **1** to those for **3**, it is more likely that the carbonyl ligand in **1** is also terminally bonded to rhenium. Moreover, the position of this CO absorption in **1** is not very different from that found for $ReH_2XCO(PR_3)_2$ (X = $SnPh_3$, $SiPh_3$) compounds[9] (ν_{CO} at 1838 cm^{-1}).

If we now consider the low-temperature NMR data for complex **2**, they are consistent with the replacement of the benzylideneimido ligand in **3** by a bridging hydride and of benzonitrile by the acetonitrile ligand. The structure we propose for **2** is shown in Scheme I. Nevertheless, it is difficult to rationalize the observed fluxionality of the hydride ligands, as only H_A and H_B are exchanging, H_C being unaffected by this phenomenon. A possible explanation could be an exchange between H_A and H_B occurring through intermediates with hydrides in terminal positions on rhenium or ruthenium, the bimetallic frame being maintained by the bridging H_C. A similar type of mechanism was proposed for the isomerization of $[Ph(PEt_3)Pt(\mu\text{-}H)_2IrH(PEt_3)_3]^+$.[10]

A summary of the observed reactivity of **1** toward the two nitriles is shown in Scheme I together with the proposed assignments of the NMR resonances.

Study of the Stoichiometric Reactivity of $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)$ (3). Reactivity toward Carbon Monoxide. Since **1** is immediately decomposed by carbon monoxide into mononuclear species,[11] we have tested the reactivity of **3** toward CO to see whether the benzylideneimido bridging ligand gives some stability to the dinuclear unit. This is indeed the case, as carbon monoxide at atmospheric pressure only replaces the benzonitrile ligand, leading to the formation of $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(CO)(PPh_3)_2$ (**4**). This formulation is supported by the disappearance in the IR spectrum of the ν_{CN} absorption and the appearance of a new band at 1946 cm^{-1} attributed to a CO group bonded to Ru, the CO bonded to Re being observed at 1798 cm^{-1}. Examination of the NMR data gathered in Table I gives evidence that the substitution

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of benzonitrile by carbon monoxide has not induced great structural changes, the coupling constants between phosphorus nuclei being very similar. The only difference is the chemical shifts of the bridging hydrides: the hydride ligand appearing at the lowest field is in a position trans to P_B, not to P_A as it is in **3**.

Reactivity toward Hydrogen. The acetonitrile ligand in **2** being easily displaced by hydrogen, it was tempting to check whether the same phenomenon was observed for **3** with the hope that, in this case, further hydrogenation of the benzylideneimido group would then occur, as has been observed for an ethylideneimido group bonded to an iron cluster.[12] In fact, the benzonitrile ligand in **3** is far less labile toward hydrogen than the acetonitrile ligand in **2** and, at room temperature and at atmospheric pressure, no reaction was observed. Under 10-atm pressure of hydrogen, **3** quantitatively reverts to **1** with liberation of benzonitrile and formation of traces of benzylamine (by GC analysis).

Let us note that **3** is a poor catalyst for the hydrogenation of benzonitrile. In tetrahydrofuran solution, under 30 atm of hydrogen and at 100 °C, benzonitrile is hydrogenated into benzylamine with a turnover of 2 h^{-1}, the substrate/catalyst ratio being 250. At the end of the reaction, **3** is not recovered and a mixture of unidentified complexes is formed, as evidenced by spectroscopic techniques. Unexpectedly, **1** has no catalytic activity under the same conditions.

In conclusion, even though the dinuclear complex **1** is electronically unsaturated, it reacts with acetonitrile to give a substitution reaction of two hydride ligands, not an addition reaction as could be expected. In the case of benzonitrile, two molecules of nitrile react and hydrometalation of one of them is observed, leading to a bridging benzylideneimido group. The origin of the difference in reactivity between these two nitriles is not clear, as the literature[3,4,12] gives examples of hydrometalation reactions for both acetonitrile and benzonitrile ligands.

Experimental Section

All experiments were performed under a nitrogen atmosphere using standard Schlenk-tube techniques. IR spectra were recorded in dichloromethane solutions on a Perkin-Elmer 225 spectrophotometer. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained on a Bruker WM 250 instrument. $ReRuH_5(CO)(PPh_3)_4$ (**1**) was synthesized by a published procedure.[1]

Synthesis of $(PPh_3)_2(CO)Re(\mu\text{-}H)_3Ru(CH_3CN)(PPh_3)_2$ (2). **1** (0.2 g) was dissolved in 10 mL of acetonitrile, and the solution was stirred for 2 h. The orange solution turned brown, and a brown precipitate slowly appeared. It was separated and recrystallized in a dichloromethane–hexane mixture, giving 0.16 g of **2** (80% yield) as brown crystals. Anal. Calcd for $C_{75}H_{66}NOP_4ReRu$: C, 63.96; H, 4.72; N, 0.99; P, 8.79; Ru, 7.18; Re, 13.22. Found: C, 63.60; H, 4.52; N, 1.12; P, 8.60; Ru, 7.46; Re, 12.14. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (except phenyl resonances) 209 (dd, CO, J = 9 and 11 Hz), 118.7 (CN), 2.9 (CH_3).

Synthesis of $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PhCN)(PPh_3)_2$ (3). To **1** (0.2 g) dissolved in THF (20 mL) was added 0.2 mL of benzonitrile (14 equiv), and the solution was stirred for 20 h at room temperature. The solution was then evaporated under vacuum to dryness, and the residue was recrystallized in a dichloromethane–hexane mixture, giving 0.15 g of **3** (65% yield) as dark green crystals. Anal. Calcd for $C_{87}H_{73}N_2OP_4ReRu$: C, 66.40; H, 4.68; N, 1.78; P, 7.87; Ru, 6.42; Re, 11.83. Found: C, 66.36; H, 4.43; N, 1.62; P, 7.61; Ru, 6.39; Re, 10.36. ^{13}C NMR (CD_2Cl_2): δ (except phenyl resonances) 207 (CO), 168.5 (d, NCHPh, J_{CH} = 156.6 Hz), 126.1 (CN).

Synthesis of $(PPh_3)_2(CO)Re(\mu\text{-}H_2)(\mu\text{-}NCHPh)Ru(CO)(PPh_3)_2$ (4). Carbon monoxide was bubbled for 1 h in a solution of **3** (0.1 g) in dichloromethane. The solution then was evaporated to dryness, and the residue was recrystallized in a dichloromethane/hexane mixture, giving 0.08 g of **4** as green crystals (83% yield). Anal. Calcd for $C_{81}H_{68}NO_2P_4ReRu$: C, 64.92; H, 4.57; N, 0.93; P, 8.27. Found: C, 64.52; H, 4.32; N, 0.84; P, 8.17.

Table III. Experimental Data for the X-ray Study of Compound 3

compd	$(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)\text{-}Ru(PPh_3)_2(NCPh)\cdot Me_2CO$
formula	$C_{90}H_{79}N_2O_2P_4ReRu$
fw	1631.82
a, Å	14.775 (2)
b, Å	23.775 (2)
c, Å	21.695 (3)
β, deg	92.53 (1)
V, Å^3	7613 (2)
Z	4
ρ_{calcd}, g cm^{-3}	1.424
space group	$C_{2h}{}^5\text{-}P2_1/n$
T, °C	22
radiation	graphite monochromated, Mo Kα, λ(Mo Kα_1) = 0.7093 Å
linear abs coeff, cm^{-1}	19.35
transmission factors[a]	0.92–0.99
receiving aperture, mm	4.0 × 4.0
takeoff angle, deg	3.5
scan speed, deg min^{-1}	2
scan mode	$\omega/2\theta$
scan range, deg	0.75 below Kα_1 to 0.75 above Kα_2
2θ limit, deg	3–40
no. of unique data used in final refinement, $F_o{}^2 > 3\sigma(F_o{}^2)$	4489
final no. of variables	299
R (on F_o, $F_o{}^2 > 3\sigma(F_o{}^2)$)[b]	0.049
R_w (on F_o, $F_o{}^2 > 3\sigma(F_o{}^2)$)[c]	0.060

[a] ψ-scan method. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$, unit weights.

Crystallographic Studies. Crystals of $(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PhCN)(PPh_3)_2$ (**3**) suitable for X-ray diffraction were obtained through recrystallization from acetone solution at −20 °C. Data were collected on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range 24° < 2θ(Mo Kα_1) < 28°. The space group was determined by careful examination of systematic extinctions in the listing of the measured reflections. Data reductions were carried out using the SDP crystallographic computing package.[13] Table III presents further crystallographic information.

The structure was solved and refined using combination of the SDP crystallographic computing package[13] and the SHELX-76 package.[14] Atomic scattering factors were taken from the usual tabulations.[15] Anomalous dispersion terms for Ru and P atoms were included in F_c.[16] An empirical absorption correction was applied.[17] Scattering factors for the hydrogen atoms were taken from Stewart et al.[18]

The positions of Re, Ru, and P atoms were determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. The compound was found to crystallize with one molecule of acetone per molecule of complex. All non-hydrogen atoms were allowed to vibrate anisotropically, except carbon atoms of the 14 phenyl rings, which were

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Table IV. Fractional Atomic Coordinates with Esd's in Parentheses for Compound 3

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Re	0.15308 (4)	0.14328 (3)	0.20041 (3)	C(72)	0.4098 (7)	0.1636 (4)	0.1448 (5)
Ru	0.02164 (8)	0.17079 (5)	0.27430 (6)	C(73)	0.4756 (7)	0.1678 (4)	0.1008 (5)
H(1)	0.087 (8)	0.119 (5)	0.265 (6)	C(74)	0.5162 (7)	0.1193 (4)	0.0787 (5)
H(2)	0.034 (8)	0.175 (5)	0.199 (6)	C(75)	0.4911 (7)	0.0666 (4)	0.1006 (5)
P(1)	0.0968 (3)	0.0769 (2)	0.1284 (2)	C(76)	0.4254 (7)	0.0624 (4)	0.1446 (5)
P(2)	0.2984 (3)	0.1080 (2)	0.2249 (2)	C(81)	0.3586 (6)	0.1435 (5)	0.2914 (4)
P(3)	0.0088 (3)	0.1530 (2)	0.3792 (2)	C(82)	0.4492 (6)	0.1600 (5)	0.2919 (4)
P(4)	−0.0576 (3)	0.2562 (2)	0.2612 (2)	C(83)	0.4912 (6)	0.1814 (5)	0.3458 (4)
C(1)	0.196 (1)	0.1795 (7)	0.1338 (8)	C(84)	0.4425 (6)	0.1863 (5)	0.3992 (4)
O(1)	0.2176 (8)	0.2053 (5)	0.0887 (6)	C(85)	0.3519 (6)	0.1697 (5)	0.3987 (4)
C(2)	0.184 (1)	0.2498 (7)	0.2897 (7)	C(86)	0.3100 (6)	0.1483 (5)	0.3448 (4)
N(2)	0.1452 (8)	0.2064 (5)	0.2661 (5)	C(91)	0.0966 (7)	0.1753 (3)	0.4369 (5)
C(3)	−0.149 (1)	0.0904 (8)	0.2537 (7)	C(92)	0.1347 (7)	0.1382 (3)	0.4806 (5)
N(3)	−0.0888 (9)	0.1211 (6)	0.2611 (6)	C(93)	0.1911 (7)	0.1587 (3)	0.5288 (5)
C(11)	0.2680 (7)	0.2779 (5)	0.2733 (4)	C(94)	0.2093 (7)	0.2162 (3)	0.5332 (5)
C(12)	0.2921 (7)	0.2810 (5)	0.2119 (4)	C(95)	0.1711 (7)	0.2532 (3)	0.4895 (5)
C(13)	0.3710 (7)	0.3091 (5)	0.1969 (4)	C(96)	0.1148 (7)	0.2327 (3)	0.4413 (5)
C(14)	0.4257 (7)	0.3342 (5)	0.2432 (4)	C(101)	−0.0933 (7)	0.1754 (5)	0.4192 (4)
C(15)	0.4016 (7)	0.3311 (5)	0.3045 (4)	C(102)	−0.1746 (7)	0.1776 (5)	0.3840 (4)
C(16)	0.3227 (7)	0.3030 (5)	0.3196 (4)	C(103)	−0.2527 (7)	0.1984 (5)	0.4098 (4)
C(21)	−0.2269 (9)	0.0562 (6)	0.2457 (5)	C(104)	−0.2495 (7)	0.2170 (5)	0.4709 (4)
C(22)	−0.2554 (9)	0.0384 (6)	0.1867 (5)	C(105)	−0.1683 (7)	0.2148 (5)	0.5061 (4)
C(23)	−0.3265 (9)	0.0000 (6)	0.1793 (5)	C(106)	−0.0902 (7)	0.1941 (5)	0.4803 (4)
C(24)	−0.3690 (9)	−0.0206 (6)	0.2308 (5)	C(111)	0.0071 (6)	0.0765 (5)	0.3924 (5)
C(25)	−0.3405 (9)	−0.0028 (6)	0.2898 (5)	C(112)	0.0796 (6)	0.0439 (5)	0.3738 (5)
C(26)	−0.2694 (9)	0.0356 (6)	0.2972 (5)	C(113)	0.0774 (6)	−0.0144 (5)	0.3804 (5)
C(31)	0.0160 (8)	0.0216 (5)	0.1489 (4)	C(114)	0.0026 (6)	−0.0402 (5)	0.4055 (5)
C(32)	−0.0387 (8)	−0.0048 (5)	0.1036 (4)	C(115)	−0.0699 (6)	−0.0077 (5)	0.4240 (5)
C(33)	−0.0983 (8)	−0.0473 (5)	0.1198 (4)	C(116)	−0.0677 (6)	0.0506 (5)	0.4174 (5)
C(34)	−0.1031 (8)	−0.0634 (5)	0.1814 (4)	C(121)	−0.1821 (7)	0.2531 (4)	0.2498 (5)
C(35)	−0.0483 (8)	−0.0370 (5)	0.2268 (4)	C(122)	−0.2139 (7)	0.2143 (4)	0.2058 (5)
C(36)	0.0112 (8)	0.0055 (5)	0.2105 (4)	C(123)	−0.3067 (7)	0.2091 (4)	0.1924 (5)
C(41)	0.0220 (7)	0.1138 (5)	0.0712 (4)	C(124)	−0.3677 (7)	0.2428 (4)	0.2229 (5)
C(42)	−0.0634 (7)	0.1300 (5)	0.0897 (4)	C(125)	−0.3359 (7)	0.2817 (4)	0.2669 (5)
C(43)	−0.1177 (7)	0.1650 (5)	0.0520 (4)	C(126)	−0.2431 (7)	0.2869 (4)	0.2803 (5)
C(44)	−0.0866 (7)	0.1838 (5)	−0.0042 (4)	C(131)	−0.0339 (6)	0.3126 (4)	0.3182 (5)
C(45)	−0.0012 (7)	0.1676 (5)	−0.0227 (4)	C(132)	−0.0761 (6)	0.3132 (4)	0.3745 (5)
C(46)	0.0531 (7)	0.1326 (5)	0.0150 (4)	C(133)	−0.0519 (6)	0.3537 (4)	0.4188 (5)
C(61)	0.3131 (7)	0.0346 (5)	0.2537 (5)	C(134)	0.0145 (6)	0.3934 (4)	0.4069 (5)
C(62)	0.3891 (7)	0.0186 (5)	0.2900 (5)	C(135)	0.0567 (6)	0.3928 (4)	0.3506 (5)
C(63)	0.3966 (7)	−0.0364 (5)	0.3122 (5)	C(136)	0.0325 (6)	0.3524 (4)	0.3063 (5)
C(64)	0.3281 (7)	−0.0753 (5)	0.2981 (5)	C(141)	−0.0373 (7)	0.2953 (5)	0.1890 (5)
C(65)	0.2522 (7)	−0.0593 (5)	0.2618 (5)	C(142)	−0.0949 (7)	0.3398 (5)	0.1725 (5)
C(66)	0.2446 (7)	−0.0043 (5)	0.2396 (5)	C(143)	−0.0842 (7)	0.3684 (5)	0.1172 (5)
C(51)	0.1734 (7)	0.0361 (4)	0.0797 (5)	C(144)	−0.0159 (7)	0.3525 (5)	0.0784 (5)
C(52)	0.2373 (7)	0.0655 (4)	0.0469 (5)	C(145)	0.0418 (7)	0.3080 (5)	0.0949 (5)
C(53)	0.2959 (7)	0.0364 (4)	0.0095 (5)	C(146)	0.0310 (7)	0.2794 (5)	0.1502 (5)
C(54)	0.2905 (7)	−0.0221 (4)	0.0050 (5)	O(s)	0.190 (2)	0.506 (2)	0.950 (2)
C(55)	0.2265 (7)	−0.0514 (4)	0.0378 (5)	C(1)(s)	0.335 (3)	0.023 (2)	0.467 (2)
C(56)	0.1680 (7)	−0.0223 (4)	0.0752 (5)	C(2)(s)	0.196 (3)	0.434 (2)	0.010 (2)
C(71)	0.3847 (7)	0.1109 (4)	0.1667 (5)	C(3)(s)	0.168 (3)	0.482 (2)	−0.010 (2)

refined as isotropic rigid groups in order to reduce the number of variable parameters (D_{6h} symmetry, C–C = 1.395 Å). Hydrogen atoms attached to the carbon atoms of phenyl rings and to C(2) were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. At this stage of the refinement, difference electron density syntheses revealed two strong peaks (x = 0.0823, y = 0.1190, z = 0.2704; x = 0.0338, y = 0.1769, z = 0.1959) situated, for the first one, at 1.97 Å from Re and 1.53 Å from Ru and, for the second one, at 1.93 Å from Re and 1.72 Å from Ru. These two peaks have been attributed to the bridging hydrides H(1) and H(2), and their positions have been refined. The hydride ligands H(1) and H(2) have also been located by the use of the program HYDEX.[19] The coordinates obtained for H(1) and H(2) (H(1), x = 0.0908, y = 0.1098, z = 0.2601; H(2), x = 0.0371, y = 0.1674, z = 0.1924) were in good agreement with the refined positions given in Table IV.

Final atomic coordinates are given in Table IV. Structure amplitudes ($10|F_o|$ vs $10|F_c|$) are available in Table S1.[20] Table S2 lists the final anisotropic thermal parameters (Å^2 × 100), and Table S3 lists the final isotropic thermal parameters (Å^2 × 100).

Registry No. 1, 134535-23-2; 2, 137966-96-2; 3, 138008-55-6; 3·Me_2CO, 138126-74-6; 4, 138008-56-7; PhCN, 100-47-0; $PhCH_2NH_2$, 100-46-9; Re, 7440-15-5; Ru, 7440-18-8; $NCHPh^-$, 138233-91-7.

Supplementary Material Available: Tables of the final anisotropic thermal parameters and the final isotropic thermal parameters for compound 3 (2 pages); a listing of final observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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[20] See paragraph at the end of the paper regarding supplementary material.