Evidence for the Lability of a Bridging Phosphido Ligand under Hydrogen Atmosphere. Reactions of the Cluster Complex $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)(CO)_8$

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Abstract: In studies to determine free organic molecules that can be derived from the coordinated acyl group of the prototype complex $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**1**) or its PR_2H substituted derivatives $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_8(PR_2H)$ (**2a**, R = C_6H_5; **2b**, R = C_6H_{11}), the species $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}PR_2)(\mu\text{-}CO)_2(CO)_6$ (**4a**, R = C_6H_5; **4b**, R = C_6H_{11}) are respectively obtained in 80% and 65% yield through a mild thermolysis of **2** where coordinated PR_2H is the source of the hydrogen atom releasing benzaldehyde. Benzene is the only organic product obtained from the reaction of **1** with H_2, producing $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**3**). By contrast, treatment of **1** with $[PPN][BH_4]$ yields benzaldehyde and the salt $[PPN][Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9]$ ($[PPN][3^*]$). The high reactivity of **4a** is first illustrated by a facile CO addition at 25 °C involving metal–metal bond opening to give the 50-e cluster $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)(CO)_9$ (**5a**) (yield, 95%). The addition of CO is reversible under reduced pressure or under a stream of argon at 25 °C. Facile ligand substitutions from **4a** are exemplified by two reactions. With triphenylphosphine, $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)(\mu\text{-}CO)_2(CO)_5(P(C_6H_5)_3)$ (**6a**) is produced in 80% yield. Reaction of **4a** with $P(C_6H_5)_2H$, by contrast, gives $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)_2(CO)_6$ (**7a**) (yield, 65%), which exists in two isomeric forms $\mathbf{7a}_1$ (symmetric) and $\mathbf{7a}_2$ (asymmetric). The latter complex is formed by rapid oxidative addition of a P–H bond of $P(C_6H_5)_2H$ to the metal, following its initial coordination. Addition of hydrogen to the title complex **4a** (tetrahydrofuran; $P(H_2)$, 40 bar; 120 °C; 2 h) promotes the conversion of the bridging phosphido group $\mu\text{-}P(C_6H_5)_2$ into a terminal $P(C_6H_5)_2H$ ligand to produce $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_8(P(C_6H_5)_2H)$ (**8a**) as the major product (yield, ca. 30%), along with three additional species identified as **3**, $\mathbf{7a}_1$, and $\mathbf{7a}_2$. Of these complexes, **8a** is reconverted to **4a** by heating under nitrogen. The formation of **3**, $\mathbf{7a}_1$, and $\mathbf{7a}_2$ bears evidence of a hydrogen assisted intermolecular redistribution of phosphido groups. All complexes are characterized by elemental analysis, infrared spectroscopy, and ^1H and ^{31}P NMR. Details of the X-ray structures of **4b**, **5a**, and **6a** are reported. The complex **4a** is a catalyst precursor for the hydrogenation of cyclohexanone (typical experiment: tetrahydrofuran, 20 mL; **4a**, 5×10^{-2} mmol; cyclohexanone, 20 mmol; $P(H_2)$, 40 bar; 120 °C; reaction time, 2 h; yield, 77%; turnover, 151).

The present state of knowledge of fundamental cluster reactions[1] allows one to rationalize the transformations of a variety of organic substrates at contiguous metal centers.[2] However, to connect this chemistry to organic synthesis and catalysis, a further goal is to release the modified substrates, which, up to now, has been rarely achieved.[3] Indeed, reductive elimination of organic molecules remains a crucial step at which many clusters fail to complete their catalytic cycle.[4]

The original intent of this study was to explore efficient means to release benzaldehyde from the prototype acyl complex $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**1**)[5,6] or its substituted derivatives $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_8(PR_2H)$ (**2a**, R = C_6H_5; **2b**, R = C_6H_{11}).[6] Acyl ligands are currently obtained from diverse reactions of alkenes with polynuclear hydrido carbonyl metal complexes[7] and are important intermediates in hydroformylation processes.[8] Since the phenyl substituent of the acyl group in **1** originates from 2-(diphenylphosphino)pyridine, the present study is also relevant to cluster-mediated degradation of phosphine ligands.[9]

During the course of the present work, we found that the coordinated PR_2H ligand in **2** can be a source of a hydrogen atom to release benzaldehyde, also providing quantitatively $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}PR_2)(\mu\text{-}CO)_2(CO)_6$ (**4a**, R = C_6H_5; **4b**, R = C_6H_{11}).

The chemistry of **4a** has been investigated. Though electronically saturated, this complex exhibits enhanced activity: it adds CO and is substituted by phosphine ligands under mild conditions; it also undergoes reversible addition of hydrogen. The results of the latter reaction shed light on the chemical reactivity of phosphido bridges in polynuclear complexes, and raise questions regarding their ability to maintain the integrity of a cluster under catalytic conditions.

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Experimental Section

General Comments. All synthetic manipulations were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Dichloromethane was distilled under nitrogen from P_2O_5 and stored under nitrogen. The following reagent grade chemicals, bis(triphenylphosphoranylidene)ammonium chloride {[PPN]Cl} (Aldrich), sodium borohydride (Aldrich), triphenylphosphine (Ega-Chemie), diphenylphosphine (Strem), and dicyclohexylphosphine (Strem), were used without further purification.

The starting complex $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**1**),[5,6] its substituted derivatives $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_8(PR_2H)$ (**2a–b**) (**2a**, R = C_6H_5; **2b**, R = C_6H_{11}),[6] and the reagent [PPN][BH_4][10] were prepared by published procedures.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer with 0.1-mm cells equipped with CaF_2 windows. ^1H and ^{31}P NMR spectra were obtained on Fourier-transform Bruker WH90 and WM250 spectrometers. ^1H NMR spectra were referenced to tetramethylsilane. ^{31}P NMR spectra were referenced to external 85% phosphoric acid. Microanalyses of C, H, N, and P elements were made by the "Service Central de Microanalyse du CNRS". Chromatographic separation of the complexes was made on silica gel columns (Kieselgel 60 Merck, 0.063–0.200 mm (70–230 mesh ASTM)). The organic substrates were analyzed by gas chromatography, using an Intersmat IGC 120 FB equipped with a column Carbowax W20M Gas Chrom Q 80/100 mesh (3 m × $^1/_8$ in.).

Preparation of the Complexes. $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (3). Procedure a. In a typical experiment, a 500-mg sample of **1** was dissolved in 40 mL of cyclohexane. A continuous hydrogen stream was bubbled through the solution which was heated under reflux for 90 min. The solution was then cooled and subsequently evaporated to dryness under vacuum. The solid residue was chromatographed on silica gel. Elution with dichloromethane/hexane (1/4) allowed the separation of two compounds: the fast moving band contained small amounts of unreacted starting material, while the second band contained the reaction product, subsequently recrystallized from dichloromethane/pentane and identified as $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**3**) (yellow crystals, 375 mg, yield 90%).

A second experiment, based on 300 mg of **1** and a reduced volume of solvent (5 mL), was designed explicitly to determine the nature of the organic product being actually released in this reaction. Analysis of the solution by gas chromatography provided evidence for benzene as the only detectable organic product.

Procedure b. A 200-mg sample of $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**1**) (0.24 mmol) was dissolved in 5 mL of THF. Addition of a stoichiometric amount of [PPN][BH_4] (131 mg, 0.24 mmol) led to a progressive color change from yellow to red. After complete dissolution of this salt (ca. 30 min), an infrared spectrum revealed the formation of an anionic complex (ν(CO) (cm^{-1}), THF) 2025 (m), 1965 (vs), 1940 (m), 1915 (m)). Analysis of the solution by gas chromatography indicated the presence of benzaldehyde as the only detectable organic product. Though the anionic complex was not fully characterized, it may be tentatively formulated as [PPN][$Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$] ([PPN][**3***]). Indeed, subsequent titration of the solution with trifluoroacetic acid provided the neutral complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**3**) which could be recovered in 76% yield after chromatographic workup. It was also verified that deprotonation of **3** by [PPN][BH_4] led to the same anionic species.

3: IR (ν(CO) (cm^{-1}), cyclohexane) 2076 (s), 2046 (vs), 2024 (vs), 2005 (s), 1983 (s), 1960 (w); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 118.1 (s, $P(C_6H_5)(C_5H_4N)$); NMR ^1H ($CDCl_3$, 25 °C) δ −15.30 (d, $^2J_{PH}$ = 25.2 Hz, hydride). Anal. Calcd for $C_{20}H_{10}N_1O_9P_1Ru_3$: C, 32.35; H, 1.36; N, 1.89; P, 4.17. Found: C, 32.47; H, 1.37; N, 2.19; P, 4.26.

$Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}PR_2)(\mu\text{-}CO)_2(CO)_6$ (4) (4a, R = C_6H_5; 4b, R = C_6H_{11}). Typical Procedure for 4a. A suspension of **2a** (1 g) in methylcyclohexane (35 mL) was heated at 90 °C for 75 min under nitrogen. The complex was rapidly dissolved and the orange color gradually turned red. The solution was then allowed to cool for 3 h, while precipitation of a red product was observed. The powder was filtered, dried under vacuum, and subsequently identified as **4a** (red powder, 735 mg, yield 80%). The complex could not be eluted from a silica gel column, even with CH_2Cl_2. Analysis of the reaction solution by gas chromatography showed benzaldehyde as the only detectable organic product.

4a: IR (ν(CO) (cm^{-1}), CH_2Cl_2) 2047 (s), 2010 (s), 1997 (s), 1970 (w), 1948 (m), 1875 (vw), 1825 (m); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 383.9 (d, $^2J_{PP}$ = 18 Hz, $P(C_6H_5)_2$), 42.0 (d, $P(C_6H_5)(C_5H_4N)$. Anal. Calcd for $C_{31}H_{19}N_1O_8P_2Ru_3$: C, 41.43; H, 2.13; N, 1.56; P, 6.89. Found: C, 42.61; H, 2.33; N, 1.56; P, 6.99.

Typical Procedure for 4b. A suspension of **2b** (500 mg) in methylcyclohexane (25 mL) was heated under reflux for 45 min. The solution was then evaporated to dryness. The product was recrystallized from dichloromethane/diethyl ether solution and subsequently characterized as **4b** (red crystals suitable for X-ray diffraction, 290 mg, yield 65%).

4b: IR (ν(CO) (cm^{-1}), CH_2Cl_2) 2040 (s), 1995 (s, br), 1965 (m), 1943 (m), 1875 (vw), 1817 (m); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 452.9 (d, $^2J_{PP}$ = 12 Hz, $P(C_6H_{11})_2$), 39.0 (d, $P(C_6H_5)(C_5H_4N)$). Anal. Calcd for $C_{31}H_{31}N_1O_8P_2Ru_3$: C, 41.65; H, 3.39; N, 1.52. Found: C, 41.29; H, 3.38; N, 1.50.

$Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)(CO)_9$ (5a). Carbon monoxide was bubbled through a dichloromethane solution (5 mL) of **4a** (200 mg) at 25 °C. A color change from red to orange was observed. Monitoring by infrared spectroscopy showed the reaction to be complete within 30 min. While the solution was kept under CO atmosphere, 15 mL of hexane were added and the Schlenk tube was cooled at −30 °C. The complex crystallized as orange air stable needles subsequently characterized as **5a** (210 mg, yield 95%). In solution, under inert atmosphere, the complex slowly reverts to **4a**.

5a: IR (ν(CO) (cm^{-1}), CH_2Cl_2) 2065 (m), 2040 (s), 2009 (m), 1995 (m), 1970 (w), 1940 (w); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 116.4 (d, $^2J_{PP}$ = 24 Hz), 7.2 (d); the complex crystallizes with 1 mol of dichloromethane. Anal. Calcd for $C_{33}H_{21}Cl_2N_1O_9P_2Ru_3$: C, 39.18; H, 2.09; N, 1.38; P, 6.12. Found: C, 40.12; H, 2.07; N, 1.39; P, 6.31.

Conversion of 5a into 4a. Argon was bubbled through a dichloromethane solution (10 mL) of **5a** (100 mg). While the orange color gradually turned red, monitoring by infrared spectroscopy indicated quantitative conversion into **4a** within 45 min.

$Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)(\mu\text{-}CO)_2(CO)_5(P(C_6H_5)_3)$ (6a). Triphenylphosphine (58 mg, 0.22 mmol) was added to a tetrahydrofuran solution (20 mL) of **4a** (200 mg, 0.22 mmol). The solution was heated at 60 °C for 2 h; a violet color was indicative of complex formation. The solvent was removed under vacuum, and the complex was recrystallized from dichloromethane/diethyl ether solution to give black crystals characterized as **6a** (204 mg, yield 80%).

6a: IR (ν(CO) (cm^{-1}), THF) 2023 (s), 1982 (s), 1925 (m), 1860 (vw), 1793 (m); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 399.1 (dd, $^2J_{P1P2}$ = 22 Hz, $^3J_{P1P3}$ = 7 Hz, $P(C_6H_5)_2$, 49.8 (dd, $^2J_{P2P3}$ = 16 Hz, $P(C_5H_4N)(C_6H_5)$), 39.9 (dd, $P(C_6H_5)_3$). Anal. Calcd for $C_{48}H_{34}N_1O_7P_3Ru_3$: C, 50.89; H, 3.02; N, 1.24; P, 8.20. Found: C, 50.63; H, 3.08; N, 1.14; P, 8.28.

$Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)_2(CO)_6$ (7a). Diphenylphosphine ($P(C_6H_5)_2H$, 37 mg, 0.22 mmol) was added to a tetrahydrofuran solution (20 mL) of **4a** (200 mg, 0.22 mmol). The solution was stirred overnight under nitrogen, while the initial red color turned orange. The solvent was removed under vacuum. Chromatographic workup on a silica gel column (heptane as eluent) led to an inseparable mixture of two complexes that were subsequently identified as isomers $\mathbf{7a}_1$ and $\mathbf{7a}_2$. When recrystallized from dichloromethane/diethyl ether, the isomer $\mathbf{7a}_1$ was obtained as the only product (yellow crystals, 143 mg, yield 63%). Some crystals of the minor isomer $\mathbf{7a}_2$ (red) were obtained by further recrystallization of the mother liquor from acetone/ethanol solution.

$\mathbf{7a}_1$ (symmetric isomer): IR (ν(CO) (cm^{-1}), CH_2Cl_2) 2032 (s), 1995 (s), 1950 (m), 1935 (s); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 251.8 (d, $^2J_{PP}$ = 15 Hz, 2 P, $P(C_6H_5)_2$), 70.5 (t, 1 P, $P(C_6H_5)(C_5H_4N)$); NMR ^1H ($CDCl_3$, 25 °C) δ −11.42 (dt, $^2J_{PH}$ = 19.1, 39.0 Hz, hydride). Anal. Calcd for $C_{41}H_{29}N_1O_6P_3Ru_3$: C, 47.91; H, 2.84; N, 1.36; P, 9.04. Found: C, 47.78; H, 2.84; N, 1.30; P, 8.97.

$\mathbf{7a}_2$ (asymmetric isomer): IR (ν(CO) (cm^{-1}), CH_2Cl_2) 2025 (s), 1997 (vs), 1980 (m), 1955 (m), 1935 (m), 1923 (m); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 268.4 (dd, $^2J_{P1P2}$ = 134 Hz, $^2J_{P1P3}$ = 15 Hz, $P(C_6H_5)_2$), 196.0 (dd, $^2J_{P2P3}$ = 74 Hz, $P(C_6H_5)_2$), 51.6 (dd, $P(C_6H_5)(C_5H_4N)$); NMR ^1H ($CDCl_3$, 25 °C) δ −10.01 (ddd, $^2J_{PH}$ = 7.4, 19.1, 29.4 Hz).

$Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_{11})_2)_2(CO)_6$ (7b). The ligand $P(C_6H_{11})_2H$ (44 mg, 0.22 mmol) was added to a tetrahydrofuran solution (20 mL) of **4b** (200 mg, 0.22 mmol). The solution was stirred overnight under nitrogen; analysis of the reaction product revealed only the existence of the symmetric isomer **7b** (178 mg, yield 75%).

7b: IR (ν(CO) (cm^{-1}), CH_2Cl_2) 2017 (s), 1980 (s), 1942 (m), 1927 (s); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 297.8 (d, $^2J_{PP}$ = 12 Hz, 2 P, $P(C_6H_{11})_2$), 61.5 (t, 1 P, $P(C_6H_5)(C_5H_4N)$); NMR ^1H ($CDCl_3$, 25 °C) δ −11.58 (dt, $^2J_{PH}$ = 17.7, 41.9 Hz). Anal. Calcd for $C_{41}H_{53}N_1O_6P_3Ru_3$: C, 46.81; H, 5.08; N, 1.33; P, 8.83. Found: C, 45.35; H, 5.08; N, 1.30; P, 8.17.

Reaction of 4a with Hydrogen. The reaction was conducted in a 100-mL laboratory reactor (a detailed description of this autoclave is given below in the section Catalytic Runs). Complex **4a** (200 mg) was

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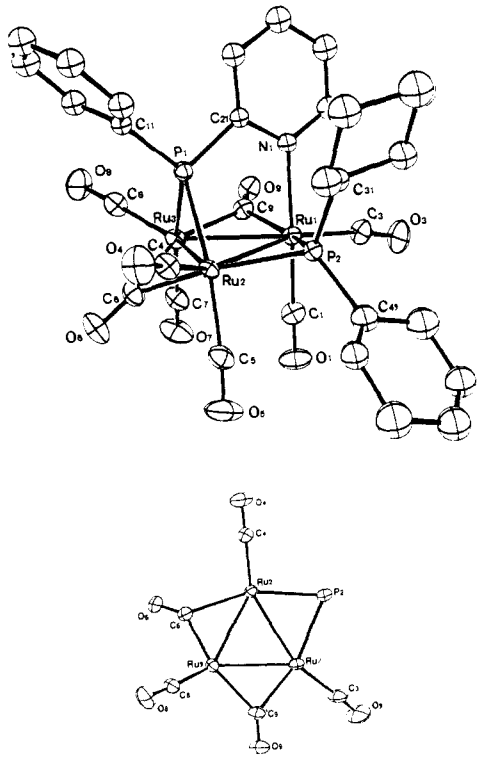


Figure 1. Perspective view of complex **4b**; a view of the principal atoms surrounding the metal triangle is shown as an insert.

dissolved in tetrahydrofuran (20 mL) under inert atmosphere. A pressure of 40 atm of H_2 was then supplied, and the reactor was thermostated at 120 °C for 2 h. The solution was then allowed to cool, and the reactor was depressurized. The solution was concentrated under vacuum and first analyzed by ^{31}P NMR. Except for one minor product appearing as traces on the spectrum (δ 144.8 (d, J_{PP} = 13 Hz), 66.3 (d)), all spectroscopically detectable species could be subsequently separated by column chromatography and characterized. The order of elution is **3**, **8a**, **7a** (inseparable mixture of $\mathbf{7a_1}$ and $\mathbf{7a_2}$). All these complexes can be prepared selectively: **7a** was obtained from the reaction of **4a** with $P(C_6H_5)_2H$ (vide supra); **3** was first isolated and characterized from the reaction of **1** with hydrogen; the new complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(P(C_6H_5)_2H)(CO)_8$ (**8a**) can be alternately prepared by the reaction of **3** with $P(C_6H_5)_2H$ (vide infra).

Conversion of 8a into 4a. The complex **8a** was quantitatively converted into the starting material **4a** upon heating in cyclohexane under reflux. The reaction was monitored by IR and was shown to be complete within 2 h.

$Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(P(C_6H_5)_2H)(CO)_8$ (8a) (alternate procedure). A tetrahydrofuran solution (20 mL) of complex $Ru_3(\mu\text{-}H)(\mu\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**3**) (200 mg, 0.27 mmol) was reacted with a stoichiometric amount of $P(C_6H_5)_2H$ (50 mg, 0.27 mmol) at 40 °C for 4 h. The yield of product **8a** after chromatographic workup (dichloromethane/hexane, 1/3) was 30%.

8a: IR (ν(CO) (cm^{-1}), cyclohexane) 2057 (s), 2022 (vs), 1995 (s), 1967 (m), 1950 (w); NMR $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C) δ 113.8 (d, $^2J_{PP}$ = 18 Hz, $P(C_6H_5)(C_5H_4N)$), 11.4 (d, $P(C_6H_5)_2H$); NMR ^1H ($CDCl_3$, 25 °C) δ 5.47 (dd, $^2J_{H1P1}$ = 9.6 Hz, J_{H1P2} = 350.5 Hz, $HP(C_6H_5)_2$), −15.31 (dd, $^2J_{H2P1}$ = 24.0 Hz, $^2J_{H2P2}$ = 10.4 Hz, hydride). Anal. Calcd for $C_{31}H_{21}N_1O_8P_2Ru_3$: C, 41.34; H, 2.35; N, 1.56; P, 6.88. Found: C, 41.24; H, 2.36; N, 1.57; P, 7.17.

Crystallographic Analyses. Crystal Data Collection and Reduction. Diffraction measurements were made on Enraf Nonius CAD4 diffractometers by using Mo Kα radiation. Unit cells were determined and refined from the setting angles of 25 randomly selected reflections within the range 12° < θ (Mo Kα) < 14°. Crystal and intensity data for compounds **4b**, **5a**, and **6a** are listed in Table I. Absorption corrections of a Gaussian integration type were done for **4b** and **5a**.

Solution and Refinement of the Structures. All calculations were performed on a VAX 11/730 by using combinations of the SDP crystallographic computing package[11] and the SHELX76 package.[12] Neutral

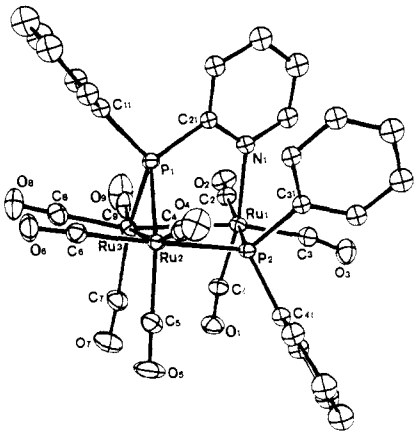


Figure 2. Perspective view of complex **5a**.

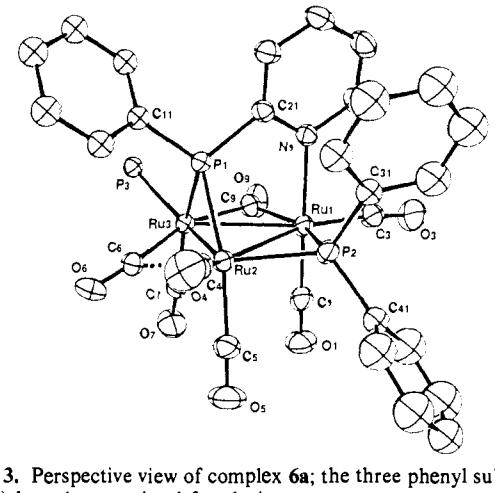


Figure 3. Perspective view of complex **6a**; the three phenyl substituents on P(3) have been omitted for clarity.

atomic scattering factors were taken from the standard sources.[13a] Anomalous dispersion corrections[13b] were applied to Ru and P atoms. All structures were solved by a combination of direct methods and difference electron density techniques, and subsequently refined by full matrix least squares, minimizing the function $\sum\omega(|F_o| - |F_c|)^2$.

Non-hydrogen atoms were refined with anisotropic thermal parameters, except for the carbon atoms of the phenyl, cyclohexyl, and pyridyl rings which were treated with isotropic thermal parameters. Hydrogen atoms were entered in idealized positions (C–H 0.95 Å) and held fixed during refinements. In the case of **6a**, phenyl rings were treated as rigid groups (idealized D_{6h} symmetry; C–C 1.395 Å, C–H 0.95 Å) in order to reduce the number of variable parameters.

Comparative lists of selected interatomic distances and bond angles for compounds **4b**, **5a**, and **6a** are given in Tables II and III. Tables of atomic coordinates, anisotropic thermal parameters, equivalent isotropic thermal parameters and tables of observed and calculated structure factor amplitudes ($10|F_o|$ vs $10|F_c|$) are available as supplementary material. Perspective views of the structures of **4b**, **5a**, and **6a** are given in Figures **1–3**.

Catalytic Runs. Hydrogenation of Cyclohexanone. All catalytic runs were performed in a 100-mL stainless-steel autoclave equipped with gas and liquid inlets, heating device, and magnetic stirring. The reactions were carried out in a Teflon vessel adjusted to the internal wall of the autoclave, thus preventing any undesirable effect of the metallic part of the reactor. The starting complex was weighted directly into the Teflon vessel. The autoclave was then closed and degased through three vacuum–argon cycles. A solution of cyclohexanone (20 mmol) in THF (20 mL) was introduced under argon, and hydrogen was admitted up to a pressure of 40 bar. At the end of each catalytic run, the autoclave was cooled with a dry ice/acetone bath and slowly vented in about 15 min.

(11) *Enraf-Nonius Structure Determination Package*, 4th ed.; Frenz B. A. & Associates, Inc.: College Station, TX 77840, and Enraf-Nonius: Delft, The Netherlands, 1981.

(12) Sheldrick, G. M. *SHELX 76, Program for Crystal Structure Determination*, University of Cambridge, Cambridge, England, 1976.

(13) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1. For hydrogen atoms, see: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

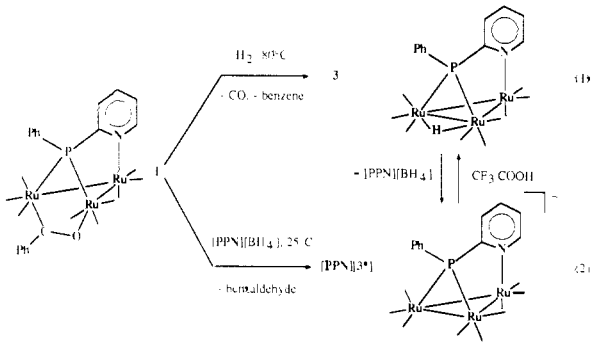
Table I. Experimental Data for X-ray Studies

	4b	5a	6a
formula	$C_{31}H_{31}N_1O_8P_2Ru_3$	$C_{33}H_{21}Cl_2O_9P_2Ru_3$	$C_{48}H_{34}N_1O_7P_3Ru_3$
F_w, amu	910.75	1011.59	1132.93
a, Å	10.430 (2)	12.263 (2)	15.807 (4)
b, Å	17.589 (4)	15.975 (3)	20.492 (4)
c, Å	9.586 (3)	10.682 (2)	14.955 (4)
α, deg	91.88 (2)	79.91 (1)	
β, deg	94.19 (2)	113.57 (1)	111.05 (2)
γ, deg	76.91 (2)	107.33 (1)	
V, Å^3	1708	1827	4521
Z	2	2	4
ρ_{calcd}, g·cm^{-3}	1.794	1.835	1.664
space group	C_i^1—$P\bar{1}$	C_i^1—$P\bar{1}$	C_{2h}^5—$P2_1/n$
crystal shape	6-sided, faces {010}, (110), {1$\bar{1}$0}, {001}	7 faces, {010}, {100}, (1$\bar{1}$0), (1$\bar{1}\bar{1}$), (1$\bar{1}$1)	
crystal vol, mm^3	0.0544	0.1082	
t, °C	20	20	20
radiation	for all three compounds, graphite monochromated, Mo Kα, λ(Mo Kα_1) = 0.7093 Å		
linear abs coeff, cm^{-1}	14.26	14.27	11.37
transmission factor	0.56–0.77	0.59–0.71	
receiving aperture, mm	2 × 4	3.5 × 4	2 × 4
take-off angle, deg	7.0	3.5	5.0
scan speed, deg min^{-1}	variable	2	variable
scan mode	ω–2θ	ω–θ	ω–2θ
scan range, deg	1.2 below Kα_1 to 1.2 above Kα_2	0.9 below Kα_1 to 0.9 above Kα_2	1.0 below Kα_1 to 1.0 above Kα_2
2θ limit, deg	3–46	3–50	3–54
unique data used in final refinement	4243	5916	6241
unique data, $F_o^2 > 3\sigma(F_o^2)$	4243	5916	6241
final no. of variables	286	331	307
R(on F_o for $F_o^2 > 3\sigma(F_o^2)$)	3.4	3.6	3.8
R_w(on F_o for $F_o^2 > 3\sigma(F_o^2)$)	3.8	5.7	3.8

A sample of the homogeneous reaction mixture was then analyzed by gas chromatography on a $^1/_8$ in. × 3 m column filled with 10% Carbowax 1540 on Chromosorb W 80–100 mesh, working at 140 °C under a nitrogen flow of 1 L/h. Yields of hydrogenated products were determined by 1,3,5-trimethylbenzene as internal standard. Results of these studies are reported in Table IV.

Results

Syntheses. Benzene is the only detectable organic compound in the treatment of $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**1**) with H_2, giving the hydrido cluster complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ (**3**) (eq 1).[9]



Treatment of **1** with [PPN][BH_4] provided only benzaldehyde, along with quantitative amounts of the anionic species [PPN][$Ru_3(\mu\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$] ([PPN][**3***]) (eq 2).[14] This "de-acylation" of **1** was found to parallel the de-protonation of **3** by [PPN][BH_4], to yield the same anionic complex [PPN][**3***].[15] Subsequent protonation of [PPN][**3***] led to complete recovery of the neutral hydrido cluster complex **3**.

While exploring alternate possibilities to generate benzaldehyde, we reasoned that the coordinated PR_2H ligand in $Ru_3(\mu\text{-}C(O)(C_6H_5))(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_8(PR_2H)$ (**2**) could eventually transfer a hydrogen atom to the acyl group via oxidative

Table II. Interatomic Distances (Å) for Compounds **4b**, **5a**, and **6a** with Esd's in Parentheses

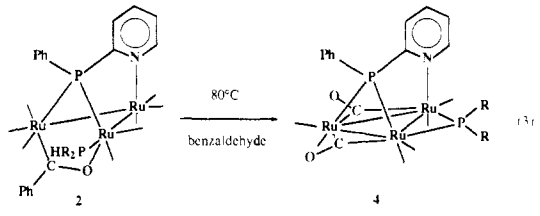
	4b	5a	6a
Ru(1)–Ru(2)	2.864 (1)	3.847 (1)[a]	2.890 (1)
Ru(1)–Ru(3)	2.830 (1)	2.916 (1)	2.824 (1)
Ru(1)–P(2)	2.363 (1)	2.409 (1)	2.351 (2)
Ru(1)–N(1)	2.170 (4)	2.197 (2)	2.212 (4)
Ru(1)–C(1)	1.870 (4)	1.865 (3)	1.855 (6)
Ru(1)–C(2)		1.944 (3)	
Ru(1)–C(3)	1.911 (5)	1.917 (3)	1.895 (6)
Ru(1)–C(9)	2.170 (4)		2.178 (8)
Ru(2)–Ru(3)	2.782 (1)	2.870 (1)	2.754 (1)
Ru(2)–P(1)	2.354 (1)	2.357 (1)	2.343 (2)
Ru(2)–P(2)	2.325 (1)	2.395 (1)	2.279 (2)
Ru(2)–C(4)	1.881 (4)	1.916 (3)	1.879 (7)
Ru(2)–C(5)	1.912 (5)	1.944 (3)	1.915 (6)
Ru(2)–C(6)	2.186 (5)	1.932 (3)	2.413 (7)
Ru(3)–P(1)	2.359 (1)	2.293 (1)	2.384 (2)
Ru(3)–P(3)			2.347 (2)
Ru(3)–C(6)	2.078 (5)		1.987 (6)
Ru(3)–C(7)	1.929 (4)	1.931 (3)	1.905 (6)
Ru(3)–C(8)	1.869 (5)	1.897 (3)	
Ru(3)–C(9)	2.131 (5)	1.906 (3)	2.114 (6)
P(1)–C(11)	1.815 (4)	1.832 (2)	1.834 (4)
P(1)–C(21)	1.813 (4)	1.834 (2)	1.805 (6)
P(2)–C(31)	1.853 (4)	1.849 (2)	1.822 (6)
P(2)–C(41)	1.850 (5)	1.837 (2)	1.818 (6)
P(3)–C(51)			1.847 (5)
P(3)–C(61)			1.840 (5)
P(3)–C(71)			1.849 (5)
N(1)–C(21)	1.344 (5)	1.351 (3)	1.353 (7)
N(1)–C(25)	1.349 (6)	1.338 (3)	1.352 (7)
C(21)–C(22)	1.387 (6)	1.386 (3)	1.395 (7)
C(22)–C(23)	1.384 (7)	1.367 (4)	1.368 (9)
C(23)–C(24)	1.363 (7)	1.362 (4)	1.381 (9)
C(24)–C(25)	1.368 (7)	1.382 (4)	1.365 (9)
⟨C–O⟩[b]	1.14 [1]	1.13 [1]	1.14 [1]
⟨C–C⟩[c]	1.37 [2]	1.38 [1]	1.395
⟨C–C⟩[d]	1.48 [3]		

[a] Nonbonding distance. [b] Within carbonyl groups. [c] Within phenyl rings. [d] Within cyclohexyl rings.

(14) (a) The structure of this anion is analogous to that of [K][Ru_3-($PPhCH_2PPh_2$)$(CO)_9$].[14b] (b) Bruce, M. I.; William, M. L.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 2557–2567.

(15) We find that [PPN][BH_4] is an excellent deprotonation agent for hydrido cluster complexes; direct use of the [PPN] salt provides an improved stabilization of the anionic species.

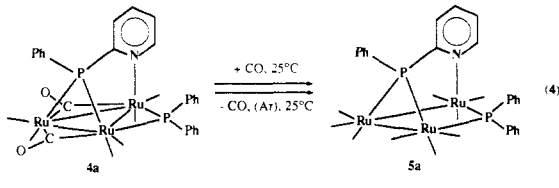
addition of a P–H bond to the metal and subsequent reductive C–H coupling.[16] Indeed, a mild thermolysis of this complex provided benzaldehyde along with quantitative amounts of the new species $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}PR_2)(\mu\text{-}CO)_2(CO)_6$ (**4**) (**4a**, R = C_6H_5; **4b**, R = C_6H_{11}) (eq 3).



(3)

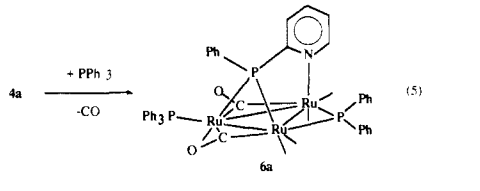
Reactions of **4a** are presented below; the isomorphous complex **4b** was introduced to provide suitable single crystals for the X-ray diffraction study. Some of the derivatives in the cyclohexyl series were also characterized (see Experimental Section).

Complex **4a** was found to add CO reversibly at 25 °C and atmospheric pressure to give the open 50-e cluster complex $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)(CO)_9$ (**5a**) (eq 4).



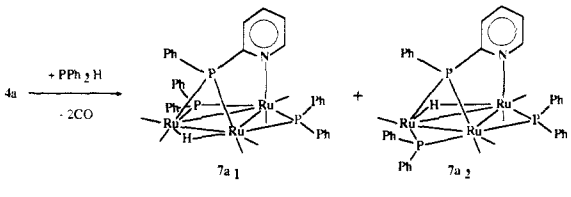
(4)

Substitution of one CO by a phosphine from **4** also proved to be a facile process: stirring a THF solution of **4a** and triphenylphosphine for 2 h at 60 °C gave **6a** (yield, 80%) (eq 5).



(5)

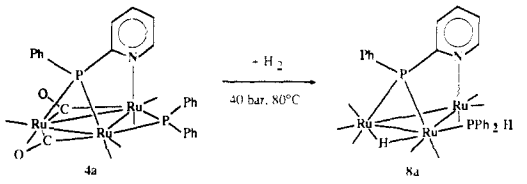
When $P(C_6H_5)_2H$ was used as the incoming phosphine, the substituted derivative was not trapped, due to its rapid conversion into the new complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)_2(CO)_6$ (**7a**) existing as two isomeric forms (eq 6).



(6)

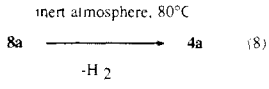
The observation of a facile P–H bond activation through the above reaction suggested that **4a** might also provide a low-energy path for the activation of other coordinated substrates. This prompted us to investigate its reaction with H_2. Under routine experimental conditions which are also those used for the hydrogenation of ketones (vide infra) ($P(H_2)$ = 40 bar; 120 °C; THF solvent) the new complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(P(C_6H_5)_2H)(CO)_8$ (**8a**) was obtained as the major product (yield, ca. 30% after 2 h) (eq 7).

The ^{31}P NMR spectrum of the solution also revealed the presence of four side products. Three of them were identified as the previously characterized species **3**, **7a**$_1$, and **7a**$_2$, (vide supra);



(7)

their formation here indicates that further de-coordination and re-distribution of the $P(C_6H_5)_2H$ ligand occurs from **8a** under the experimental conditions of this reaction. The reaction of **4a** with hydrogen was found to be partially reversible, since quantitative conversion of **8a** into **4a** with evolution of H_2 was achieved within 90 min in refluxing cyclohexane (eq 8). The complex **8a** could be alternately obtained selectively from the reaction of **3** with $P(C_6H_5)_2H$.



(8)

Spectroscopic and Crystallographic Characterization of the Complexes. The basic structure of all complexes reported here consists of a trimetal ruthenium framework capped with a face-bridging ligand, as shown previously for **1** and **2** by crystallographic means.[6]

The structure of complex **3** was inferred by analogy of its IR and NMR spectra with those of the isostructural complexes $Ru_3(\mu\text{-}H)(\mu_3\text{-}X(C_6H_5)CH_2X(C_6H_5)_2)(CO)_9$ (X = As[14b] or P[17]).

The structure of $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_{11})_2)(\mu\text{-}CO)_2(CO)_6$ (**4b**) has been determined in this work (Figure 1). It shows a closed trimetal geometry (Ru(1)–Ru(2) = 2.864 (1) Å; Ru(1)–Ru(3) = 2.830 (1) Å; Ru(2)–Ru(3) = 2.782 (1) Å); an additional phosphido group, derived from the terminal $P(C_6H_{11})_2H$ ligand of the antecedent species **2b**, spans a different edge than the first one and occupies an equatorial position (dihedral angle {Ru(1)–Ru(2)–Ru(3)}–{Ru(1)–Ru(2)–P(2)} = 9.1°). It is noteworthy that all three metal centers of this 48-e species are hepta-coordinated, whereas two equatorial carbonyl groups are in a bridging position. A view of the principal atoms surrounding the metal triangle is shown as an insert in Figure 1. The terminally bonded CO groups in this projection each define a coordination axis which intersects the center of the metal triangle (in planar projection). Such a feature may also be seen in the related compound $Ru_3(\mu\text{-}C_2Bu\text{-}t)(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6$.[18]

The ^{31}P NMR spectra of **4a** contains a rather surprising low-field resonance[19] (δ 383.9, d, $^2J_{PP}$ = 18 Hz) which is assigned by comparison with the spectrum of complex **6a** (see Experimental Section and Figure 3). An unambiguous assignment can be made for the spectrum of **6a** owing to the presence of an additional phosphorus atom, P(3). In the latter, the phosphorus atom of the $P(C_6H_5)(C_5H_4N)$ group, P(1), is the only one with two independent phosphorus neighbors in cis position, and the assignment can be made on the basis of the values of the coupling constants $J_{(P-P)}$. Thus, the low-field resonance in this case can be assigned to the equatorial PPh_2 group; δ P(2) = 399.1 (dd, $^2J_{P1P2}$ = 22 Hz, $^3J_{P2P3}$ = 7 Hz); the two other phosphorus resonances appear in the normal region (49.8 and 39.9 ppm). The unusually low field resonance in **4a** mentioned above is thus similarly assigned to the PPh_2 group; in **4b** this resonance is seen at δ = 452.9 ppm (d, $^2J_{PP}$ = 12 Hz, assigned to PCy_2).

Returning to the structure of **6a** (Figure 3), it is remarkable that replacement of a CO ligand by a triphenylphosphine ligand causes no significant modification in the overall geometry of the

(16) (a) Related H transfers from PR_2H to coordinated alkylidyne,[16b] or to coordinated alkynes,[16c] have been observed; sequential reduction of a hydrocarbyl with a primary phosphine has been also reported,[16d] though the desorbed alkane was not traced in this experiment. (b) Jeffery, J. C.; Lawrence-Smith, J. G. *J. Chem. Soc., Chem. Commun.* **1985**, 275–277. (c) Jeffery, J. C.; Smith, J. G. *J. Chem. Soc., Chem. Commun.* **1986**, 17–19. (d) Kwek, K.; Taylor, N. J.; Carty, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 4636–4638.

(17) Lugan, N.; Bonnet, J.-J.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4484–4491.

(18) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27–C32.

(19) (a) It has been suggested[19b] that the chemical shift of a bridging phosphido group is dependent on the metal–phosphorus–metal angle. A notable exception is found here in **4b**: in spite of analogous angle Ru(2)–P(1)–Ru(3) 72.34 (3)° and Ru(1)–P(2)–Ru(2) 75.36 (4)°, one of the two ^{31}P signals is shifted in the low-field region where phosphinidene groups are usually expected. (b) Carty, A. J. *Top. Stereochem.*, in press.

Table III. Bond Angles (deg) for Compounds **4b**, **5a**, and **6a** with Esd's in Parentheses

	4b	5a	6a		4b	5a	6a
Ru(2)-Ru(1)-Ru(3)	58.49 (1)		57.61 (1)	Ru(2)-Ru(3)-C(6)	51.0 (1)		58.6 (2)
Ru(2)-Ru(1)-P(2)	51.66 (3)		50.26 (4)	Ru(2)-Ru(3)-C(7)	114.8 (1)	92.04 (9)	107.3 (3)
Ru(2)-Ru(1)-N(1)	95.9 (1)		92.5 (2)	Ru(2)-Ru(3)-C(8)	137.0 (2)	96.21 (8)	
Ru(2)-Ru(1)-C(1)	83.9 (2)		87.8 (2)	Ru(2)-Ru(3)-C(9)	110.3 (1)	163.5 (1)	112.2 (2)
Ru(2)-Ru(1)-C(3)	156.3 (2)		156.6 (3)	P(1)-Ru(3)-P(3)			100.28 (6)
Ru(2)-Ru(1)-C(9)	106.3 (2)		105.5 (2)	P(1)-Ru(3)-C(6)	85.2 (1)		81.8 (2)
Ru(3)-Ru(1)-P(2)	109.64 (3)	83.77 (2)	107.66 (4)	P(1)-Ru(3)-C(7)	168.40 (2)	145.2 (1)	160.8 (3)
Ru(3)-Ru(1)-N(1)	90.6 (1)	92.89 (5)	92.2 (2)	P(1)-Ru(3)-C(8)	97.7 (2)	90.29 (8)	
Ru(3)-Ru(1)-C(1)	86.5 (2)	75.35 (8)	88.0 (3)	P(1)-Ru(3)-C(9)	96.3 (1)	112.4 (1)	104.8 (2)
Ru(3)-Ru(1)-C(2)		91.93 (8)		P(3)-Ru(3)-C(6)			106.0 (2)
Ru(3)-Ru(1)-C(3)	143.1 (2)	167.90 (8)	145.4 (3)	P(3)-Ru(3)-C(7)			96.7 (3)
Ru(3)-Ru(1)-C(9)	48.3 (1)		47.9 (2)	P(3)-Ru(3)-C(9)			88.7 (2)
P(2)-Ru(1)-N(1)	88.8 (1)	83.91 (5)	86.1 (2)	C(6)-Ru(3)-C(7)	87.9 (1)		85.0 (3)
P(2)-Ru(1)-C(1)	93.6 (2)	94.11 (8)	94.1 (2)	C(6)-Ru(3)-C(8)	101.4 (3)		
P(2)-Ru(1)-C(2)		170.37 (8)		C(6)-Ru(3)-C(9)	154.6 (2)		162.7 (3)
P(2)-Ru(1)-C(3)	107.1 (2)	91.41 (8)	107.0 (3)	C(7)-Ru(3)-C(8)	92.8 (3)	92.4 (1)	
P(2)-Ru(1)-C(9)	153.9 (2)		155.4 (2)	C(7)-Ru(3)-C(9)	86.1 (2)	102.3 (1)	84.3 (3)
N(1)-Ru(1)-C(1)	176.8 (1)	168.2 (1)	179.7 (5)	C(8)-Ru(3)-C(9)	103.5 (3)	91.5 (1)	
N(1)-Ru(1)-C(2)		97.72 (9)		Ru(2)-P(1)-Ru(3)	72.34 (3)	76.04 (2)	71.25 (4)
N(1)-Ru(1)-C(3)	93.7 (1)	97.6 (1)	90.7 (3)	Ru(2)-P(1)-C(11)	120.5 (1)	116.84 (8)	122.5 (2)
N(1)-Ru(1)-C(9)	79.1 (2)		92.1 (3)	Ru(2)-P(1)-C(21)	120.9 (2)	121.88 (8)	116.6 (3)
C(1)-Ru(1)-C(2)		93.12 (1)		Ru(3)-P(1)-C(11)	127.3 (1)	121.77 (8)	120.3 (2)
C(1)-Ru(1)-C(3)	87.8 (2)	94.0 (1)	89.1 (3)	Ru(3)-P(1)-C(21)	112.6 (1)	120.11 (8)	117.5 (2)
C(1)-Ru(1)-C(9)	97.9 (1)		87.8 (3)	C(11)-P(1)-C(21)	102.6 (1)	100.7 (1)	106.1 (2)
C(2)-Ru(1)-C(3)		94.4 (1)		Ru(1)-P(2)-Ru(2)	75.36 (4)	106.39 (2)	77.24 (6)
C(3)-Ru(1)-C(9)	96.8 (2)		97.5 (3)	Ru(1)-P(2)-C(31)	118.3 (2)	106.79 (7)	121.7 (2)
Ru(1)-Ru(2)-Ru(3)	60.16 (1)		59.98 (2)	Ru(1)-P(2)-C(41)	118.9 (2)	117.40 (8)	117.7 (2)
Ru(1)-Ru(2)-P(1)	72.77 (3)		73.64 (4)	Ru(2)-P(2)-C(31)	117.5 (2)	115.40 (7)	118.5 (2)
Ru(1)-Ru(2)-P(2)	52.98 (3)		52.51 (5)	Ru(2)-P(2)-C(41)	117.2 (2)	113.14 (8)	121.9 (2)
Ru(1)-Ru(2)-C(4)	154.4 (1)		150.0 (3)	C(31)-P(2)-C(41)	107.4 (3)	97.8 (1)	100.5 (3)
Ru(1)-Ru(2)-C(5)	103.2 (2)		99.4 (2)	Ru(3)-P(3)-C(51)			117.8 (2)
Ru(1)-Ru(2)-C(6)	103.6 (1)		103.5 (2)	Ru(3)-P(3)-C(61)			114.9 (2)
Ru(3)-Ru(2)-P(1)	53.92 (3)	50.82 (2)	55.05 (4)	Ru(3)-P(3)-C(71)			116.1 (2)
Ru(3)-Ru(2)-P(2)	112.59 (3)	85.02 (2)	112.24 (5)	C(51)-P(3)-C(61)			102.4 (2)
Ru(3)-Ru(2)-C(4)	133.1 (1)	164.49 (7)	141.6 (3)	C(51)-P(3)-C(71)			101.6 (2)
Ru(3)-Ru(2)-C(5)	110.1 (1)	94.70 (9)	102.8 (3)	C(61)-P(3)-C(71)			101.6 (2)
Ru(3)-Ru(2)-C(6)	47.6 (2)	87.96 (7)	44.6 (2)	Ru(1)-N(1)-C(21)	119.6 (3)	122.3 (2)	120.1 (4)
P(1)-Ru(2)-P(2)	96.94 (4)	86.45 (2)	98.78 (6)	Ru(1)-N(1)-C(25)	122.7 (3)	119.5 (2)	121.9 (4)
P(1)-Ru(2)-C(4)	97.6 (1)	113.74 (8)	101.9 (2)	C(21)-N(1)-C(25)	117.7 (4)	118.2 (2)	117.5 (5)
P(1)-Ru(2)-C(5)	163.6 (1)	145.45 (9)	157.6 (3)	Ru(2)-C(6)-Ru(3)	81.4 (2)		76.8 (2)
P(1)-Ru(2)-C(6)	83.0 (2)	88.42 (7)	74.5 (2)	Ru(2)-C(6)-O(6)	137.8 (4)		128.1 (6)
P(2)-Ru(2)-C(4)	106.6 (1)	93.09 (8)	100.6 (3)	Ru(3)-C(6)-O(6)	139.8 (4)		154.2 (6)
P(2)-Ru(2)-C(5)	92.7 (2)	88.38 (8)	93.1 (2)	Ru(1)-C(9)-Ru(3)	82.3 (2)		82.3 (3)
P(2)-Ru(2)-C(6)	154.5 (1)	172.91 (7)	155.7 (2)	Ru(1)-C(9)-O(9)	139.3 (4)		135.9 (5)
C(4)-Ru(2)-C(5)	92.3 (1)	100.6 (1)	94.5 (3)	Ru(3)-C(9)-O(9)	138.2 (4)		140.0 (6)
C(4)-Ru(2)-C(6)	98.6 (2)	93.4 (1)	103.7 (3)	P(1)-C(21)-C(22)	125.2 (4)	122.8 (2)	126.0 (4)
C(5)-Ru(2)-C(6)	82.7 (1)	93.1 (1)	86.9 (3)	P(1)-C(21)-N(1)	112.6 (3)	116.4 (2)	112.3 (4)
Ru(1)-Ru(3)-Ru(2)	61.36 (1)	83.34 (1)	62.41 (2)	N(1)-C(21)-C(22)	122.14 (5)	120.8 (2)	121.6 (5)
Ru(1)-Ru(3)-P(1)	73.34 (3)	78.97 (2)	74.37 (4)	N(1)-C(25)-C(24)	122.9 (5)	123.0 (3)	123.3 (6)
Ru(1)-Ru(3)-P(3)			132.43 (4)	C(21)-C(22)-C(23)	118.7 (5)	120.1 (3)	119.5 (6)
Ru(1)-Ru(3)-C(6)	107.8 (2)		119.4 (2)	C(22)-C(23)-C(24)	119.3 (5)	119.3 (3)	119.1 (6)
Ru(1)-Ru(3)-C(7)	100.1 (2)	100.79 (9)	100.4 (2)	C(23)-C(24)-C(25)	119.3 (6)	118.7 (3)	119.0 (6)
Ru(1)-Ru(3)-C(8)	148.4 (2)	166.94 (9)		⟨Ru-C-O⟩[a]	176 [3]	175 [4]	176 [2]
Ru(1)-Ru(3)-C(9)	49.4 (2)	85.88 (9)	49.9 (2)	⟨C-C-C⟩[b]	120 [1]	120 [1]	120
Ru(2)-Ru(3)-P(1)	53.74 (3)	53.14 (2)	53.69 (4)	⟨C-C-C⟩[c]	115 [3]		
Ru(2)-Ru(3)-P(3)			149.12 (4)				

[a] Within carbonyl groups excluding C(6)O(6) and C(9)O(9) for compounds **3b** and **5a**. [b] Within phenyl rings. [c] Within cyclohexyl rings.

complex. By contrast, dramatic geometric changes occur when **4a** accommodates an additional CO ligand to give the 50-e cluster complex $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)(CO)_9$ (**5a**) (Figure 2). The metal–metal separation Ru(1)···Ru(2) becomes nonbonding (Ru(1)···Ru(2) = 3.847 (1) Å) and the bridging carbonyls (in **4a**) have shifted to terminal position. We now see the ^{31}P NMR resonance of phosphido groups in the expected range.[19b]

The main geometric features of the 48-e species **4** are seen in the two isomers of **7**.[20] The structure of these complexes is related to that of **4** by a replacement of the bridging carbonyls C(6)–O(6) and C(9)–O(9) in the latter by a bridging hydride ligand and a bridging phosphido group in the two isomers of **7**. The isomers differ in the distribution of these μ-H and a μ-PR_2 groups over the two available metal–metal edges Ru(1)–Ru(3) and Ru(2)–Ru(3). The major isomer is the symmetric one **7a**, and it appears the less crowded. In the case of complex **7b**, containing the bulky cyclohexyl group, only one isomer, the symmetric one $\mathbf{7b_1}$, is seen.

Although we were not able to get single crystals of complex **8a**, its structure could be unambiguously derived from spectroscopic data: the existence of a terminal $P(C_6H_5)_2H$ ligand was inferred from the chemical shift of the phosphorus nuclei and from the characteristic value of the coupling constant J_{PH} = 350 Hz; the position of this ligand was deduced from the value of the coupling constant $^2J_{PP}$ = 18 Hz, characteristic of a cis arrangement of phosphorus atoms relative to the metal.

Discussion

Contrasts in Elimination of Benzene and Benzaldehyde. The differences between reactions given in eq 1 and 2 are worth noting.

(20) The X-ray structures of $\mathbf{7b_1}$ and $\mathbf{7a_2}$ have been determined (Lugan, N. Thèse de Doctorat d'Etat es Sciences, Universitē Paul Sabatier, Toulouse, 1987) and will be published separately.

Table IV. Results of the Catalytic Hydrogenation of Cyclohexanone in the Presence of Complex **4a** or Related Species[a]

catalyst precursor	T (°C)	time (h)	yield (%)	turnover rate (h^{-1})
4a	30	4.5	1	0
4a	43	6	1.5	0
4a	80	6	8	6
4a	120	1	31	120
4a	120	2	77	151
4a	120	4	83	100
4a[b]	120	5	87	146
4a	120	6	88	62
4b	120	6	8	6
3	120	4	1	0
7a	120	4	58	46

[a] Experimental conditions: THF, 20 mL; catalyst precursor, 5×10^{-2} mmol; cyclohexanone, 20 mmol; $P(H_2)$, 40 bar. [b] 20 mmol of cyclohexanone added after 2.5 h; the added substrate is hydrogenated at the same rate.

In the former case, dissociative loss of CO must precede oxidative addition of hydrogen to the metal;[21] de-insertion of the acyl group must then be favored in the coordinatively unsaturated intermediate, leading to the product benzene.[22] On the other hand, nucleophilic attack of H^- on the cluster most likely occurs via an associative path in which an unsaturated intermediate is avoided, as is migratory de-insertion. This illustrates that the sequence of nucleophilic (H^-) and electrophilic (H^+) attack may yield different products on a cluster than that of the reaction with molecular hydrogen, even when the final complexes may be identical. In reaction 2, the hydride may well attack directly at the electropositive carbon of the acyl group.

The thermally induced hydrogen atom transfer from a coordinated PR_2H ligand to the acyl group (eq 3) leading to the formation of benzaldehyde may be of valuable interest as a means to promote the elimination of an organic substrate from a metal cluster.[16] It is noteworthy that intramolecular oxidative addition of a P–H bond to the metal involves two electrons, while reductive elimination of a C–H bond and further de-coordination of the acyl group involves four electrons. The resulting unsaturation is balanced by formation of a metal–metal bond to yield the closed 48-e cluster complex $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}PR_2)(\mu\text{-}CO)_2(CO)_6$ (**4**).

Enhanced Reactivity of the Saturated 48e⁻ Complex 4a. The high reactivity of **4a** toward CO and phosphine ligands brings it into the family of electronically saturated metal clusters for which a facile and reversible metal–metal edge opening can be observed under mild conditions in the presence of nucleophiles.[18,23-27] As a member of this family, **4a** shows structural features that may account for its enhanced reactivity: the presence of two bridging phosphido groups leads to a highly distorted geometry about metal centers; such a strained structure can be only lightly stabilized through carbonyl bridges (all three metal centers in **4a** show heptacoordination) and may enter in a tautomeric equilibrium with an open species (involving terminal carbonyl ligands) that can be trapped by either CO or a phosphine ligand. The kinetics of such a phenomenum have been recently studied by Huttner[25] and Vahrenkamp[26] in related examples. The equilibrium between closed and open species is sensitive to slight steric and/or electronic effects. This is indicated in the present complexes by the reluctance of **4b** (where the bridging ligand is $P(C_6H_{11})_2$) to give a stable adduct **5b** under 1 atm of carbon monoxide.

One may reasonably suggest that the formation of type **6a** substituted derivatives also involves the intermediacy of an open adduct (not detected here) which subsequently loses CO. It is noteworthy that the coordination site of the phosphine ligand in **6a** is Ru(3), while the opened edge in the CO adduct **5a** is Ru(1)–Ru(2).

The structural features that are believed to account for the high reactivity of **4a** are also observed in $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)(\mu\text{-}CO)_2(CO)_5(P(C_6H_5)_3)$ (**6a**). Thus, facile metal–metal edge opening within type **6** substituted derivatives may also provide a vacant coordination site permitting subsequent transformation of the coordinated substrate. This occurs when $P(C_6H_5)_2H$ is the incoming ligand: the labile substituted derivative is not observed in that case, due to its rapid conversion into $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}P(C_6H_5)_2)_2(CO)_6$ (**7a**) via oxidative addition of the P–H bond to the metal (eq 6).

Reversible Transformation of μ-$P(C_6H_5)_2$ in η^1-$P(C_6H_5)_2H$ under Hydrogen. Complex **4a** reacts reversibly with molecular hydrogen without CO loss to give $Ru_3(\mu\text{-}H)(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(CO)_8(P(C_6H_5)_2H)$ (**8a**). This is rare even for unsaturated species.[28] Reaction of a cluster with hydrogen normally requires loss of CO as the initial step,[22] unless a vacant coordination site is provided by lowering the hapticity of a bridging ligand.[29]

To date, related bridge elimination reactions have never been observed in the presence of molecular hydrogen, but they have been obtained in some instances upon nucleophilic attack by H^-,[30] protonation,[31] or through diverse coupling reactions.[17,32] The reverse reaction, i.e., the conversion of a terminal PR_2H ligand into a bridging phosphido group, is more currently observable; it may involve concurrent metal–metal bond opening,[33] loss of CO,[34] and less commonly evolution of H_2.[35] The existence of three side products in the forward reaction with H_2, namely, complexes **3**, **7a**$_1$, and **7a**$_2$, bears evidence for further intermolecular redistribution of phosphido groups. Whether this occurs via de-coordination of $P(C_6H_5)_2H$ or via transient intermolecular oxidative addition of a P–H bond is not known.

Catalytic Hydrogenation of Cyclohexanone in the Presence of 4a. Complex **4a** is a catalyst precursor for the hydrogenation of cyclohexanone. At the present stage of our investigation, we have no kinetic data to ascertain a truly cluster catalyzed reaction. Nevertheless, the preliminary results reported in Table IV are of interest in that the hydrogenation of cyclohexanone is not currently achieved by mononuclear ruthenium complexes.[36] These results

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deserve the following comments: (i) the efficiency of **4a** as a catalyst precursor becomes significant above 80 °C, with an optimized activity at 120 °C; the reaction rates are matching those previously reported for $H_4Ru_4(CO)_{12}$;[37] (ii) the identification of the complexes present in solution at the end of catalytic runs reveals a product distribution analogous with that observed under hydrogen and in the absence of organic substrate (namely, **8a**, **3**, and **7a** vide supra); (iii) the efficiency of this system cannot be attributed to the formation of the side products **3** and **7a**; these complexes show only very low activity when they are prepared separately and used as catalyst precursors; (iv) complex **4b** (cyclohexyl derivative) is much less efficient than **4a**; this may be related to the fact that ligand addition to this complex via metal–metal bond opening is much less favorable than for the phenyl derivative, due to the steric bulk of cyclohexyl groups; indeed, we have previously noted above the reluctance of **4b** to give a CO adduct under ambient conditions.

Conclusion

The phosphido-bridged cluster complex $Ru_3(\mu_3\text{-}P(C_6H_5)(C_5H_4N))(\mu\text{-}PR_2)(\mu\text{-}CO)_2(CO)_6$ combines a high substitutional lability with the ability to add hydrogen reversibly through the unusual opening of a phosphido bridge. This may reflect a comparable magnitude of the energies required for metal–metal and metal–phosphorus edge opening processes.[38] Labile metal–metal interactions may be due to the strained geometry imposed by bridging phosphido ligands. Elimination of a phosphido bridge under hydrogen can reform the terminal PR_2H ligand. Other observations in this paper provide evidence that transfer of hydrogen from a PR_2H ligand to a coordinated organic group will result in the formation of a free organic molecule. Thus, the elementary steps of a catalytic cycle may be constructed from the stoichiometric reactions that have been traced here; they may serve to model the catalytic hydrogenation of cyclohexanone which has been effectively accomplished.

While the assistance of flexible ligands donating a variable number of electrons to a cluster may help to stabilize reactive intermediates in homogeneous catalysis,[3h,i] the present work suggests that bridging phosphido groups also possess a certain degree of flexibility and may serve as hydrogen "reservoir" through transient $P(C_6H_5)_2H$ intermediates. However, the facile intermolecular redistribution of $P(C_6H_5)_2H$ also indicates that stabilization of a cluster framework by bridging phosphido groups cannot be taken for granted as soon as the complex is under hydrogen atmosphere.

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Registry No. 1, 99641-43-7; **2a**, 106500-80-5; **2b**, 106500-81-6; **3**, 99583-07-0; [PPN]**3***, 115141-09-8; **4a**, 115141-03-2; **4b**, 115141-04-3; **5a**, 115141-13-4; **6a**, 115141-05-4; $\mathbf{7a}_1$, 115141-06-5; $\mathbf{7a}_2$, 115141-07-6; **7b**, 115141-10-1; **8a**, 115141-11-2; cyclohexanone, 25512-62-3; benzene, 71-43-2; benzaldehyde, 100-52-7; diphenylphosphine, 829-85-6.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and equivalent isotropic thermal parameters for **4b**, **5a**, and **6a** (10 pages); complete listings of observed and calculated structure factor amplitudes for **4b**, **5a**, and **6a** (89 pages). Ordering information is given on any current masthead page.

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