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

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Abstract: In studies to determine free organic molecules that can be derived from the coordinated acyl group of the prototype $complex Ru_3(\mu-C(O)(C_6H_5))(\mu_3-P(C_6H_5)(C_5H_4N))(CO)_9 (1) \text{ or its } PR_2H \text{ substituted derivatives } Ru_3(\mu-C(O)(C_6H_5))(\mu_3-P(C_$ $P(C_6H_5)(C_5H_4N)(CO)_8(PR_2H)$ (2a, $R = C_6H_5$; 2b, $R = C_6H_{11}$), the species $Ru_3(\mu_3 - P(C_6H_5)(C_5H_4N))(\mu - PR_2)(\mu - CO)_2(CO)_6$ $(4a, R = C_6H_5; 4b, R = C_6H_{11})$ 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 H₂, producing $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(CO)_9$ (3). By contrast, treatment of 1 with [PPN][BH₄] yields benzaldehyde and the salt [PPN][Ru₃(μ_3 -P(C₆H₃)(C₅H₄N))(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 Ru₃(μ_3 -P-(C₆H₅)(C₅H₄N))(μ -P(C₆H₅)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, $Ru_{3}(\mu_{3}-P(C_{6}H_{5})(C_{5}H_{4}N))(\mu-P(C_{6}H_{5})_{2})(\mu-CO)_{2}(CO)_{5}(P(C_{6}H_{5})_{3})$ (6a) is produced in 80% yield. Reaction of 4a with $P(C_{6}H_{5})_{2}H_{5}$. by contrast, gives $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(\mu-P(C_6H_5)_2)_2(CO)_6$ (7a) (yield, 65%), which exists in two isomeric forms 7a₁ (symmetric) and 7a₂ (asymmetric). The latter complex is formed by rapid oxidative addition of a P-H bond of P(C₆H₅)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 μ -P(C₆H₅)₂ into a terminal P(C₆H₅)₂H ligand to produce $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(CO)_8(P(C_6H_5)_2H)$ (8a) as the major product (yield, ca. 30%), along with three additional species identified as 3, 7a₁, and 7a₂. Of these complexes, 8a is reconverted to 4a by heating under nitrogen. The formation of 3, 7a₁, and 7a₂ bears evidence of a hydrogen assisted intermolecular redistribution of phosphido groups. All complexes are characterized by elemental analysis, infrared spectroscopy, and ¹H and ³¹P 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 reactions¹ 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."

The original intent of this study was to explore efficient means to release benzaldehyde from the prototype acyl complex Ru₃- $(\mu$ -C(O)(C₆H₅)) $(\mu_3$ -P(C₆H₅)(C₅H₄N))(CO)₉ (1)^{5,6} or its substituted derivatives $Ru_3(\mu-C(O)(C_6H_5))(\mu_3-P-(C_6H_5)(C_5H_4N))(CO)_8(PR_2H)$ (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 complexes⁷ 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.⁵

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 $Ru_3(\mu_3$ -P- $(C_6H_5)(C_5H_4N))(\mu - PR_2)(\mu - CO)_2(CO)_6$ (4a, R = C₆H₅; 4b, R $= C_6 H_{11}$).

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 $Ru_3(\mu-C(O)(C_6H_5))(\mu_3-P(C_6H_5)(C_5H_4N))$ -(CO)₉ (1),^{5,6} its substituted derivatives $Ru_3(\mu-C(O)(C_6H_5))(\mu_3-P-(C_6H_5)(C_5H_4N))(CO)_8(PR_2H)$ (2a-b) (2a, $R = C_6H_5$; 2b, $R = C_6H_{11})$,⁶ and the reagent [PPN][BH₄]¹⁰ were prepared by published procedures.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer with 0.1-mm cells equipped with CaF₂ windows. ¹H and ³¹P NMR spectra were obtained on Fourier-transform Bruker WH90 and WM250 spectrometers. ¹H NMR spectra were referenced to tetramethylsilane. ³¹P 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. $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_3H_4N))(CO)_9$ (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 $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(CO)_9$ (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.

A 200-mg sample of $Ru_3(\mu$ -C(O)(C₆H₅))(μ_3 -P-Procedure b. $(C_6H_5)(C_5H_4N))(CO)_9$ (1) (0.24 mmol) was dissolved in 5 mL of THF. Addition of a stoichiometric amount of [PPN][BH₄] (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][Ru₃(μ_3 -P- $(C_6H_5)(C_5H_4N))(CO)_9]$ ([PPN][3*]). Indeed, subsequent titration of the solution with trifluoroacetic acid provided the neutral complex $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(CO)_9$ (3) which could be recovered in 76% yield after chromatographic workup. It was also verified that deprotonation of 3 by [PPN][BH₄] 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 ³¹P{¹H} (CDCl₃, 25 °C) δ 118.1 (s, $P(C_6H_5)(C_5H_4N)$; NMR ¹H (CDCl₃, 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. Ru₃(μ_3 -P(C₆H₅)(C₅H₄N))(μ -PR₂)(μ -CO)₂(CO)₆ (d) (4a, R = C₆H₅; Hz, hydride) C, Automatic C, 20, (1.0) in the second s

 $Ru_3(\mu_3 - P(C_6H_5)(C_5H_4N))(\mu - PR_2)(\mu - CO)_2(CO)_6$ (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), CH₂Cl₂) 2047 (s), 2010 (s), 1997 (s), 1970 (w), 1948 (m), 1875 (vw), 1825 (m); NMR ³¹P{¹H} (CDCl₃, 25 °C) δ

383.9 (d, ${}^{2}J_{PP}$ = 18 Hz, $P(C_{6}H_{5})_{2}$), 42.0 (d, $P(C_{6}H_{5})(C_{5}H_{4}N)$. Anal. Calcd for $C_{31}H_{19}N_{1}O_{8}P_{2}Ru_{3}$: 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), CH₂Cl₂) 2040 (s), 1995 (s, br), 1965 (m), 1943 (m), 1875 (vw), 1817 (m); NMR ³¹P[¹H] (CDCl₃, 25 °C) δ 452.9 (d, ²J_{PP} = 12 Hz, *P*(C₆H₁₁)₂), 39.0 (d, *P*(C₆H₅)(C₅H₄N)). Anal. Calcd for C₃₁H₃₁N₁O₈P₂Ru₃: C, 41.65; H, 3.39; N, 1.52. Found: C, 41.29; H, 3.38; N, 1.50.

Ru₃(μ_3 -P(C₆H₅)(C₅H₄N))(μ -P(C₆H₅)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), CH₂Cl₂) 2065 (m), 2040 (s), 2009 (m), 1995 (m), 1970 (w), 1940 (w); NMR ³¹Pl¹H} (CDCl₃, 25 °C) δ 116.4 (d, ²J_{PP} = 24 Hz), 7.2 (d); the complex crystallizes with 1 mol of dichloromethane. Anal. Calcd for C₃₃H₂₁Cl₂N₁O₃P₂Ru₃: 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.

Ru₃(μ_3 -**P**(C₆H₅)(C₅H₄**N**))(μ -**P**(C₆H₅)₂)(μ -**CO**)₂(**CO**)₅(**P**(C₆H₅)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 ³¹P[¹H] (CDCl₃, 25 °C) δ 399.1 (dd, ²J_{P1P2} = 22 Hz, ³J_{P1P3} = 7 Hz, P(C₆H₅)₂, 49.8 (dd, ²J_{P2P3} = 16 Hz, P(C₅H₄N)(C₆H₅)), 39.9 (dd, P(C₆H₅)₃). Anal. Calcd for C₄₈H₃₄N₁O₇P₃Ru₃: 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.

 $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(\mu-P(C_6H_5)_2)_2(CO)_6$ (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 7a₁ and 7a₂. When recrystallized from dichloromethane/diethyl ether, the isomer 7a₁ was obtained as the only product (yellow crystals, 143 mg, yield 63%). Some crystals of the minor isomer 7a₂ (red) were obtained by further recrystallization of the mother liquor from acetone/ethanol solution.

7a₁ (symmetric isomer): IR (ν (CO) (cm⁻¹), CH₂Cl₂) 2032 (s), 1995 (s), 1950 (m), 1935 (s); NMR ³¹P{¹H} (CDCl₃, 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 (CDCl₃, 25 °C) δ -11.42 (dt, ²J_{PH} = 19.1, 39.0 Hz, hydride). Anal. Calcd for C₄₁H₂₉N₁O₆P₃Ru₃: 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.

7a₂ (asymmetric isomer): IR (ν (CO) (cm⁻¹), CH₂Cl₂) 2025 (s), 1997 (vs), 1980 (m), 1955 (m), 1935 (m), 1923 (m); NMR ³¹Pl¹H] (CDCl₃, 25 °C) δ 268.4 (dd, ²J_{P1P2} = 134 Hz, ²J_{P1P3} = 15 Hz, *P*(C₆H₅)₂), 196.0 (dd, ²J_{P2P3} = 74 Hz, *P*(C₆H₅)₂), 51.6 (dd, *P*(C₆H₅)(C₅H₄N)); NMR ¹H (CDCl₃, 25 °C) δ -10.01 (ddd, ²J_{PH} = 7.4, 19.1, 29.4 Hz). **Ru**₃(μ -H)(μ ₃-**P**(C₆H₅)(C;H₄N))(μ -P(C₆H₁)₁)₂)(CO)₆ (7b). The lig-

 $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(\mu-P(C_6H_{11})_2)_2(CO)_6$ (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%).

The initial product of the symmetric bound of (176 mg, yield 178). 7b: IR (ν (CO) (cm⁻¹), CH₂Cl₂) 2017 (s), 1980 (s), 1942 (m), 1927 (s); NMR ³¹P[¹H] (CDCl₃, 25 °C) δ 297.8 (d, ²J_{PP} = 12 Hz, 2 P, P-(C₆H₁₁)₂), 61.5 (t, 1 P, P(C₆H₅)(C₅H₄N)); NMR ¹H (CDCl₃, 25 °C) δ -11.58 (dt, ²J_{PH} = 17.7, 41.9 Hz). Anal. Calcd for C₄₁H₅₃N₁O₆P₃Ru₃: 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 ³¹P 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 $7a_1$ and $7a_2$). 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 $Ru_3(\mu-H)(\mu_3-P (C_{6}H_{5})(C_{5}H_{4}N))(P(C_{6}H_{5})_{2}H)(CO)_{8}$ (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

 $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(P(C_6H_5)_2H)(CO)_8$ (8a) (alternate procedure). A tetrahydrofuran solution (20 mL) of complex $Ru_3(\mu$ - $H_{1}(\mu - P(C_{6}H_{5})(C_{5}H_{4}N))(CO)_{9}$ (3) (200 mg, 0.27 mmol) was reacted with a stoichiometric amount of P(C₆H₅)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 ³¹P[¹H} (CDCl₃, 25 °C) δ 113.8 (d, ²J_{PP} = 1967 (m), 1950 (w); (MMK 2 H; (CDCl₃, 25 C) 6 H ³.8 (d, 3 5 H = 18 Hz, $P(C_{6}H_{5})(C_{5}H_{4}N))$, 11.4 (d, $P(C_{6}H_{5})_{2}H)$; NMR ¹H (CDCl₃, 25 °C) 6 5.47 (dd, $^{2}J_{H1P1} = 9.6$ Hz, $J_{H1P2} = 350.5$ Hz, $HP(C_{6}H_{5})_{2}$), -15.31 (dd, $^{2}J_{H2P1} = 24.0$ Hz, $^{2}J_{H2P2} = 10.4$ Hz, hydride). Anal. Calcd for $C_{31}H_{21}N_{1}O_{8}P_{2}Ru_{3}$: 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 K α radiation. Unit cells were determined and refined from the setting angles of 25 randomly selected reflections within the range $12^{\circ} < \theta$ (Mo K α) < 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 package¹¹ 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 $\sum \omega (|F_0| - |F_c|)^2$.

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 $(10|F_0| \text{ vs } 10|F_0|)$ 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 De-

⁽¹²⁾ Shedher, O. M. SHELZ YO, Program for Crystal Shedher 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)
<i>b</i> , 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
Ζ	2	2	4
$\rho_{\rm calcd}, \rm g \cdot \rm cm^{-3}$	1.794	1.835	1.664
space group	$C_i^1 - P\overline{1}$	$C_i^1 - P\overline{1}$	$C_{2h}^{5} - P_{2_{1}}/n$
crystal shape	6-sided, faces {010}, (110), {110}, {001}	7 faces, $\{010\}$, $\{100\}$, $(1\overline{1}0)$, $(1\overline{1}\overline{1})$, $(1\overline{1}1)$	
crystal vol, mm ³	0.0544	0.1082	
t, °C	20	20	20
radiation	for all three compounds, gr	aphite monochromated. Mo Ka	$\lambda(M_0 K \alpha_1) = 0.7093 \text{ Å}$
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	$\omega - 2\theta$	$\omega - \theta$	$\omega - 2\theta$
scan range, deg	1.2 below $K\alpha_1$ to	0.9 below $K\alpha_1$ to	1.0 below $K\alpha_1$ to
	1.2 above $K\alpha_2$	0.9 above $\dot{K}\alpha_2$	1.0 above \mathbf{K}_{α_2}
2θ limit, deg	3-46	3-50	3-54
unique data used in final refinement	4243	5916	6241
unique data, $F_0^2 > 3\sigma(F_0^2)$	4243	5916	6241
final no. of variables	286	331	307
$R(\text{on } F_{o} \text{ for } F_{o}^{2} > 3\sigma(F_{o}^{2}))$	3.4	3.6	3.8
$R_{\rm w}({\rm on}\ F_{\rm o}\ {\rm for}\ F_{\rm o}^2 > 3\sigma(F_{\rm o}^2))$	3.8	5.7	3.8

A sample of the homogeneous reaction mixture was then analyzed by gas chromatography on a 1/8 in. \times 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 $Ru_3(\mu-C(O)(C_6H_5))(\mu_3-P-(C_6H_5)(C_5H_4N))(CO)_9$ (1) with H₂, giving the hydrido cluster complex $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(CO)_9$ (3) (eq 1).⁹



Treatment of 1 with [PPN][BH₄] provided only benzaldehyde, along with quantitative amounts of the anionic species [PPN]-[Ru₃(μ -P(C₆H₅)(C₅H₄N))(CO)₉] ([PPN][3*]) (eq 2).¹⁴ This "de-acylation" of 1 was found to parallel the de-protonation of 3 by [PPN][BH₄], 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 $Ru_3(\mu$ -C-

(14) (a) The structure of this anion is analogous to that of [K][Ru₃-(PPhCH₂PPh₂)(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][BH₄] is an excellent deprotonation agent for buddied cluster completes of the [DPI] column for the structure of the structure

(15) We find that [PPN][BH₄] is an excellent deprotonation agent for hydrido cluster complexes; direct use of the [PPN] salt provides an improved stabilization of the anionic species. Table II. Interatomic Distances (Å) for Compounds 4b, 5a, and 6a with Esd's in Parentheses

$\begin{array}{c c c c c c c c c c c c c c c c c c c $		4b	5a	6a	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1)-Ru(2)	2.864 (1)	$3.847 (1)^a$	2,890 (1)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1) - Ru(3)	2.830 (1)	2.916 (1)	2.824 (1)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1) - P(2)	2.363 (1)	2.409 (1)	2.351 (2)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1) - N(1)	2.170 (4)	2.197 (2)	2.212 (4)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1) - C(1)	1.870 (4)	1.865 (3)	1.855 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1)-C(2)	.,	1.944 (3)		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1)-C(3)	1.911 (5)	1.917 (3)	1.895 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1) - C(9)	2.170 (4)		2.178 (8)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(2)-Ru(3)	2.782 (1)	2.870(1)	2.754 (1)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(2) - P(1)	2.354 (1)	2.357 (1)	2.343 (2)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(2)-P(2)	2.325 (1)	2.395 (1)	2.279 (2)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(2)-C(4)	1.881 (4)	1.916 (3)	1.879 (7)	
$\begin{array}{c ccccc} Ru(2)-C(6) & 2.186 (5) & 1.932 (3) & 2.413 (7) \\ Ru(3)-P(1) & 2.359 (1) & 2.293 (1) & 2.384 (2) \\ Ru(3)-P(3) & & 2.347 (2) \\ Ru(3)-C(6) & 2.078 (5) & 1.987 (6) \\ Ru(3)-C(7) & 1.929 (4) & 1.931 (3) & 1.905 (6) \\ Ru(3)-C(8) & 1.869 (5) & 1.897 (3) \\ Ru(3)-C(9) & 2.131 (5) & 1.906 (3) & 2.114 (6) \\ P(1)-C(11) & 1.815 (4) & 1.832 (2) & 1.834 (4) \\ P(1)-C(21) & 1.813 (4) & 1.834 (2) & 1.805 (6) \\ P(2)-C(31) & 1.853 (4) & 1.849 (2) & 1.822 (6) \\ P(2)-C(41) & 1.850 (5) & 1.837 (2) & 1.818 (6) \\ P(3)-C(51) & & 1.840 (5) \\ P(3)-C(61) & & 1.840 (5) \\ N(1)-C(22) & 1.344 (5) & 1.351 (3) & 1.353 (7) \\ N(1)-C(22) & 1.349 (6) & 1.338 (3) & 1.352 (7) \\ C(21)-C(22) & 1.387 (6) & 1.386 (3) & 1.395 (7) \\ C(22)-C(24) & 1.363 (7) & 1.362 (4) & 1.361 (9) \\ C(23)-C(24) & 1.363 (7) & 1.382 (4) & 1.365 (9) \\ C(24)-C(25) & 1.368 (7) & 1.382 (4) & 1.365 (9) \\ C(2-C)^{c} & 1.37 [2] & 1.38 [1] & 1.395 \\ (C-C)^{d} & 1.48 [3] \end{array}$	Ru(2)-C(5)	1.912 (5)	1.944 (3)	1.915 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(2)-C(6)	2.186 (5)	1.932 (3)	2.413 (7)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(3) - P(1)	2.359 (1)	2.293 (1)	2.384 (2)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(3)-P(3)			2.347 (2)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(3)-C(6)	2.078 (5)		1.987 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(3)-C(7)	1.929 (4)	1.931 (3)	1.905 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(3)-C(8)	1.869 (5)	1.897 (3)		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(3)-C(9)	2.131 (5)	1.906 (3)	2.114 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	P(1)-C(11)	1.815 (4)	1.832 (2)	1.834 (4)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	P(1) - C(21)	1.813 (4)	1.834 (2)	1.805 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	P(2)-C(31)	1.853 (4)	1.849 (2)	1.822 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	P(2)-C(41)	1.850 (5)	1.837 (2)	1.818 (6)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	P(3) - C(51)			1.847 (5)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	P(3)-C(61)			1.840 (5)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	P(3)-C(71)			1.849 (5)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	N(1)-C(21)	1.344 (5)	1.351 (3)	1.353 (7)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1)-C(25)	1.349 (6)	1.338 (3)	1.352 (7)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(21)-C(22)	1.387 (6)	1.386 (3)	1.395 (7)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(22) - C(23)	1.384 (7)	1.367 (4)	1.368 (9)	
$\begin{array}{cccc} C(24)-C(25) & 1.368 \ (7) & 1.382 \ (4) & 1.365 \ (9) \\ (C-O)^{b} & 1.14 \ [1] & 1.13 \ [1] & 1.14 \ [1] \\ (C-C)^{c} & 1.37 \ [2] & 1.38 \ [1] & 1.395 \\ (C-C)^{d} & 1.48 \ [3] \end{array}$	C(23) - C(24)	1.363 (7)	1.362 (4)	1.381 (9)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(24) - C(25)	1.368 (7)	1.382 (4)	1.365 (9)	
$(C-C)^{a}$ 1.3/[2] 1.38 [1] 1.395 $(C-C)^{d}$ 1.48 [3]	$(C-O)^{\nu}$	1.14 [1]	1.13 [1]	1.14 [1]	
	$(\mathbf{U} - \mathbf{U})^{\mathbf{v}}$	1.3/[2]	1.38 [1]	1.395	
	(L-L)-	1.48 [3]			

^aNonbonding distance. ^bWithin carbonyl groups. ^cWithin phenyl rings. ^dWithin cyclohexyl rings.

 $(O)(C_6H_5))(\mu_3-P(C_6H_5)(C_5H_4N))(CO)_8(PR_2H)$ (2) could eventually transfer a hydrogen atom to the acyl group via oxidative

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 $Ru_3(\mu_3-P(C_6H_5)(C_5H_4N))(\mu-PR_2)(\mu-CO)_2(CO)_6$ (4) 4a, $R = C_6H_5$; 4b, $R = C_6H_{11}$ (eq 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 $Ru_3(\mu_3-P(C_6H_5)(C_5H_4N))(\mu-P(C_6H_5)_2)(CO)_9$ (5a) (eq 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).



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 $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(\mu-P(C_6H_5)_2)_2(CO)_6$ (7a) existing as two isomeric forms (eq 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 H₂. Under routine experimental conditions which are also those used for the hydrogenation of ketones (vide infra) $(P(H_2) = 40 \text{ bar}; 120 \,^{\circ}\text{C}; \text{THF}$ solvent) the new complex $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-P}(\text{C}_6\text{H}_5)(\text{C}_5\text{H}_4\text{N}))(\text{P}(\text{C}_6\text{H}_5)_2\text{H})(\text{CO})_8$ (**8a**) was obtained as the major product (yield, ca. 30% after 2 h) (eq 7).

The ³¹P 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);



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 $P(C_6H_5)_2H$.

Spectroscopic and Crystallographic Characterization of the Complexes. The basic structure of all complexes reported here consists of a trimetal ruthenium framework capped with a facebridging 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 $Ru_3(\mu-H)(\mu_3-X(C_6H_5)CH_2X(C_6H_5)_2)(CO)_9$ (X = As^{14b} or P¹⁷).

The structure of $Ru_3(\mu_3 - P(C_6H_5)(C_5H_4N))(\mu - P(C_6H_{11})_2)(\mu$ - $CO_2(CO)_6$ (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 $\{Ru(1)-Ru(2)-Ru(3)\}-\{Ru(1)-Ru(2)-P(2)\} = 9.1^{\circ}\}$. 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 $Ru_3(\mu-C_2Bu-t)(\mu-PPh_2)(\mu-CO)_2(CO)_6$.¹⁸

The ³¹P NMR spectra of 4a contains a rather surprising lowfield resonance¹⁹ (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 PPh₂ group; $\delta P(2) = 399.1$ (dd, ${}^{2}J_{P1P2} = 22$ Hz, ${}^{3}J_{P2P3} = 7$ 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 PPh₂ group; in **4b** this resonance is seen at $\delta = 452.9$ 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 PR₂H 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 suggested¹⁹⁶ 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 ³¹P 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

anan	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)		1(0 7 (0)
P(2)-Ru(1)-C(2)		170.37 (8)		C(6) - Ru(3) - C(9)	154.6 (2)	00 4 (1)	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)	04.2 (2)
P(2) - Ru(1) - C(9)	153.9 (2)	1 (0 0 (1)	155.4 (2)	C(7) - Ru(3) - C(9)	86.1 (2)	102.3(1)	84.3 (3)
N(1)-Ru(1)-C(1)	1/6.8 (1)	168.2 (1)	1/9.7 (5)	C(8) - Ru(3) - C(9)	103.5(3)	91.5 (1)	71.25 (4)
N(1) - Ru(1) - C(2)	02.7(1)	97.72 (9)	007(2)	Ru(2) - P(1) - Ru(3)	12.34(3)	76.04 (2)	/1.25 (4)
N(1) - Ru(1) - C(3)	93.7 (1)	97.0(1)	90.7 (3)	Ru(2) - P(1) - C(11)	120.5(1)	110.84 (8)	122.5(2)
N(1) - Ru(1) - C(9)	/9.1 (2)	02.12.(1)	92.1 (3)	Ru(2) - P(1) - C(21)	120.9(2)	121.00 (0)	110.0(3) 120.3(2)
C(1) = Ru(1) = C(2)	979 (7)	93.12(1)	80 1 (2)	Ru(3) - P(1) - C(11) Ru(3) - P(1) - C(21)	127.5(1)	121.77(6) 120.11(8)	120.3(2) 117.5(2)
C(1) = Ru(1) = C(3)	07.0 (2)	94.0 (1)	07.1 (3) 97.9 (3)	C(11) = P(1) = C(21)	112.0(1)	120.11(0) 100.7(1)	117.3(2) 1061(2)
$C(2) = \mathbf{R}_{11}(1) = C(3)$	<i>37.3</i> (1)	044(1)	07.0 (3)	$P_{1}(1) = P_{1}(1) = C_{2}(21)$	75.36(4)	106.39 (2)	77 24 (6)
C(2) = Ru(1) = C(3)	96.8 (2)	<u>74.4</u> (1)	07 5 (3)	$R_{u}(1) = P(2) = C(31)$	1183(2)	106.39 (2)	121.7(2)
$R_{\rm H}(1) - R_{\rm H}(2) - R_{\rm H}(3)$	60.6(2)		50.08 (2)	$R_{u}(1) = P(2) = C(31)$	118.9(2)	11740(8)	121.7(2) 1177(2)
$R_{u}(1) - R_{u}(2) - P(1)$	7277(3)		73 64 (4)	$R_{u}(2) - P(2) - C(31)$	1175(2)	117.40(0) 115.40(7)	117.7(2) 118 5 (2)
$R_{u}(1) - R_{u}(2) - P(2)$	52.98 (3)		52 51 (5)	$R_{11}(2) = P(2) = C(41)$	117.3(2) 117.2(2)	113.40(7)	121.9(2)
Ru(1) - Ru(2) - C(4)	1544(1)		150.0 (3)	C(31)-P(2)-C(41)	1074(3)	97 8 (1)	100.5(3)
Ru(1) - Ru(2) - C(5)	103.2(2)		994(2)	$R_{11}(3) - P(3) - C(51)$	10).1 (5)	y/.0 (1)	100.5(3)
Ru(1) - Ru(2) - C(6)	103.2(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)	107 0 (0)		132.43 (4)	C(21)-C(22)-C(23)	118.7 (5)	120.1 (3)	119.5 (6)
Ku(1)-Ku(3)-C(6)	107.8 (2)	100 50 (0)	119.4 (2)	C(22)-C(23)-C(24)	119.3 (5)	119.3 (3)	119.1 (6)
Ku(1) - Ku(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)	(0.0.(0))	$(Ru-C-O)^{\alpha}$	176 [3]	175 [4]	176 [2]
Ku(1) - Ku(3) - C(9)	49.4 (2)	85.88 (9)	49.9 (2)	$(U-U-U)^{o}$	120 [1]	120 [1]	120
KU(2) - KU(3) - P(1) Pu(2) = Pu(2) = P(2)	55.74 (5)	53.14 (2)	33.69 (4)	(L-L-L) [,]	115 [3]		
KU(2) - KU(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 $Ru_3(\mu_3-P(C_6H_5)(C_5H_4N))(\mu-P(C_6H_5)_2)(CO)_9$ (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 ³¹P 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 -PR₂ 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 **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 $7b_1$ and $7a_2$ have been determined (Lugan, N. Thèse de Doctorat d'Etat es Sciences, Université 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	<i>T</i> (°C)	time (h)	yield (%)	turnover rate (h ⁻¹)
4a	30	4.5	1	0
4 a	43	6	1.5	0
4 a	80	6	8	6
4a	120	1	31	120
4 a	120	2	77	151
4 a	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
7 a	120	4	58	46

^aExperimental 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 inter-mediate, 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 $\operatorname{Ru}_3(\mu_3-\operatorname{P}(C_6H_5)(C_5H_4N))(\mu-\operatorname{PR}_2)(\mu-\operatorname{PR}_$ $CO)_2(CO)_6$ (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 Huttner²⁵ and Vahrenkamp²⁶ 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 $Ru_3(\mu_3-P (C_6H_5)(C_5H_4N))(\mu - P(C_6H_5)_2)(\mu - CO)_2(CO)_5(P(C_6H_5)_3)$ (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 $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(\mu-P(C_6H_5)_2)_2$ $(CO)_{6}$ (7a) via oxidative addition of the P-H bond to the metal (eq 6).

Reversible Transformation of μ -P(C₆H₅)₂ in η^1 -P(C₆H₅)₂H under Hydrogen. Complex 4a reacts reversibly with molecular hydrogen without CO loss to give $Ru_3(\mu-H)(\mu_3-P(C_6H_5)(C_5H_4N))(CO)_8$ - $(P(C_6H_5)_2H)$ (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 PR₂H 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 H₂.³⁵ The existence of three side products in the forward reaction with H₂, 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 $Ru_3(\mu_3$ -P- $(C_6H_5)(C_5H_4N))(\mu$ -PR₂) $(\mu$ -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; **7a**₁, 115141-06-5; **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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