

In related work it has been noted that correlations of this type but with E_{em} rather than E_{00} gave correlations that are statistically less significant and slopes that are far less.^{2,3a} The major difference between the correlations with E_{em} and E_{00} is that E_{em} includes contributions from the vibrational modes, which vary as E_{00} .

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Supplementary Material Available: Listings of displacement parameters, bond lengths, and bond angles (8 pages). Ordering information is given on any current masthead page.

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Cluster-Promoted Cleavage of a Phosphorus-Carbon Bond under Ambient Conditions. Synthesis, Structure, and Stereospecific Substitution Reactions of the Acyl Cluster Complex $Ru_3(\mu-\eta^2-C(O)(C_6H_5))(\mu_3-\eta^2-P(C_6H_5)(C_5H_4N))(CO)_9$

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The monosubstituted complex $Ru_3(CO)_{11}(PPh_2py)$ (1), prepared from $Ru_3(CO)_{12}$ and diphenylpyridylphosphine PPh_2py by using $[PPN]CN$ as a catalyst, experiences a spontaneous P-C bond-cleavage reaction at 25 °C. The expelled phenyl substituent undergoes migratory CO insertion to yield the acyl complex $Ru_3(\mu-\eta^2-C(O)(C_6H_5))(\mu_3-\eta^2-P(C_6H_5)(C_5H_4N))(CO)_9$ (2) (yield, 85%). The high reactivity observed for 2 is related to a stereospecific labilizing effect of the acyl group toward adjacent carbonyl ligands. This is exemplified by its reaction with several phosphines at 30 °C, leading to $Ru_3(\mu-\eta^2-C(O)(C_6H_5))(\mu_3-\eta^2-P(C_6H_5)(C_5H_4N))(CO)_8(L)$ (3) (3a, L = PPh_3 ; 3b, L = PPh_2H ; 3c, L = PCy_2H). The X-ray structures of 2 and 3a are reported. Crystal data for $Ru_3(\mu-\eta^2-C(O)(C_6H_5))(\mu_3-\eta^2-P(C_6H_5)(C_5H_4N))(CO)_9$ (2): orthorhombic, space group $P2_12_12_1$, $a = 10.431$ (2) Å, $b = 15.888$ (5) Å, $c = 17.821$ (5) Å, $V = 2953$ Å³, $Z = 4$. Full-matrix least-squares refinement of 379 variables for 2757 reflections with $F_o^2 > 3\sigma(F_o^2)$ led to $R = 0.043$ and $R_w = 0.049$. Crystal data for $Ru_3(\mu-\eta^2-C(O)(C_6H_5))(\mu_3-\eta^2-P(C_6H_5)(C_5H_4N))(CO)_8(P(C_6H_5)_3)$ (3a): monoclinic, space group $P2_1/n$, $a = 10.650$ (3) Å, $b = 31.023$ (4) Å, $c = 13.016$ (2) Å, $\beta = 97.57(2)^\circ$, $V = 4262$ Å³, $Z = 4$. Full-matrix least-squares refinement of 383 variables for 5770 observations with $F_o^2 > 3\sigma(F_o^2)$ led to $R = 0.049$ and $R_w = 0.087$. Both these triangular 50-e cluster complexes are edge double-bridged species, with an acyl group $C(O)(C_6H_5)$ and a phenylpyridylphosphido group $P(C_6H_5)(C_5H_4N)$ spanning the open metal-metal vector $Ru(2)-Ru(3)$. Additional coordination of the nitrogen atom of the pyridyl substituent on phosphorus to the unique ruthenium atom $Ru(1)$ confers on the latter ligand a key role in preserving the integrity of the metal cluster. In the monosubstituted derivatives 3, the phosphine ligand occupies an equatorial coordination site, in a cis position relative to the oxygen of the acyl group.

Introduction

Recent years have seen considerable success in various attempts to bring about the reaction of clusters under mild conditions.¹ For a long time, investigators in ruthenium cluster chemistry have been looking for ruthenium complexes able to duplicate the rich chemistry available to osmium through reactive species, either unsaturated, like $Os_3(\mu-H)_2(CO)_{10}$,² or lightly stabilized, like $Os_3(CO)_{12-n}(CH_3CN)_n$ ($n = 1, 2$).³ Success has been recently obtained in the preparation of $Ru_3(CO)_{12-n}(CH_3CN)_n$,⁴ permitting the activation of various substrates at or below ambient temperature. Alternately, discoveries of catalytic systems⁵⁻⁷ for

substitution of CO by phosphine ligands in $Ru_3(CO)_{12}$ have provided a rapid and quantitative access to monosubstituted cluster complexes $Ru_3(CO)_{11}(PR_3)$, which were not readily available in high yield through thermal routes.

Following our recent studies of the cluster-assisted transformations of bis(diphenylphosphino)methane,^{8,9} we used diphenylpyridylphosphine as an alternate edge-bridging ligand, with the aim to induce a site specificity within a ruthenium triangle. Earlier studies¹⁰ of the thermal reaction of this ligand with $Ru_3(CO)_{12}$ led to isolation of the trisubstituted complex $Ru_3(CO)_9(PPh_2py)_3$ (along with monomeric species), in agreement with previous observations that monosubstitution is the rate-determining step.¹¹ By using published catalytic procedures,^{5,6} we were able to isolate the monosubstituted derivative $Ru_3(CO)_{11}(PPh_2py)$ (1) quantitatively. This species is the precursor for the title complex $Ru_3(\mu-\eta^2-C(O)(C_6H_5))(\mu_3-\eta^2-P(C_6H_5)(C_5H_4N))(CO)_9$ (2). Though electronically saturated, this complex possesses important features that one would like to design into a cluster:

- (1) Lavigne, G.; Kaesz, H. D. In *Clusters and Catalysis*; Gates, B. C.; Guzzi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; Chapter IV.
- (2) Adams, R. D.; Selegue, J. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. IV, p 1023.
- (3) (a) Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *124*, C19. (b) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmüdt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064. (c) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407. (d) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1982**, 233.
- (4) Foulds, G. A.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *296*, 147.
- (5) Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321.
- (6) (a) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647. (b) The catalytic system involving highly dissociated salts has recently been elucidated and extended to the case of $[PPN]BH_4$ and various hydride donors: Lavigne, G.; Lugan, N.; Bonnet, J. J., submitted for publication.

- (7) Aime, S.; Botta, M.; Gobetto, R.; Osella, D. *Organometallics* **1985**, *4*, 1475.
- (8) Lugan, N.; Bonnet, J.-J.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4484.
- (9) Bergounhou, C.; Bonnet, J.-J.; Fompeyrine, P.; Lavigne, G.; Lugan, N.; Mansilla, F. *Organometallics* **1986**, *5*, 60 and references therein.
- (10) Maisonnat, A.; Farr, J. P.; Olmstead, M. M.; Hunt, C.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 3961.
- (11) (a) Candlin, J. P.; Shortland, A. C. *J. Organomet. Chem.* **1969**, *16*, 289. (b) Poë, A.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860. (c) Keeton, D. P.; Malik, S. K.; Poë, A. *J. Chem. Soc., Dalton Trans.* **1977**, 233. (d) Malik, S. K.; Poë, A. *Inorg. Chem.* **1978**, *17*, 1484.

face-bridging ligand to prevent fragmentation; presence of an acyl group with CO stabilizing properties that allow substitutions to take place at ambient temperature, with site specificity. A preliminary communication of this work has appeared.¹²

Experimental Section

General Comments. All synthetic manipulations were performed under a nitrogen atmosphere by using standard Schlenk-line techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Dichloromethane was distilled under nitrogen from P₂O₅, and stored under nitrogen. The following reagent grade chemicals, bis(triphenylphosphoranylidene)ammonium chloride ([PPN]Cl, Aldrich), sodium cyanide (Ega-Chemie), triphenylphosphine (Ega-Chemie), diphenylphosphine (Strem), dicyclohexylphosphine (Strem), and ruthenium trichloride (RuCl₃·nH₂O, Johnson Matthey) were used without further purification. P(C₆H₅)₂(C₃H₄N),¹⁰ Ru₃(CO)₁₂,¹³ and [PPN]CN¹⁴ were prepared by published procedures.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer using 0.1-mm cells equipped with CaF₂ windows. All spectra were calibrated against water vapor absorptions. ¹H, ³¹P, and ¹³C NMR spectra were obtained on Fourier-transform Bruker WH90 and WM250 spectrometers. ¹H and ¹³C NMR spectra were referenced to tetramethylsilane. ³¹P NMR spectra were referenced to external 85% phosphoric acid. Microanalyses of C, H, N, and P were made by the "Service Central de Microanalyse du CNRS". Chromatographic workup was performed on silica gel 60 (70–230 mesh ASTM, Merck) with columns 2.5 cm² × 30 cm.

Syntheses. Ru₃(CO)₁₁(PPh₂py) (1). The preparation of this complex was achieved by using the catalytic procedure involving [PPN]CN⁶ (we verified that the alternate procedure involving sodium benzophenone ketyl⁵ could be also used in this case and led to comparable yields of product). The reaction was conducted under nitrogen in a 100-mL Schlenk flask. Ru₃(CO)₁₂ (0.5 g, 0.78 mmol) and diphenylpyridylphosphine (0.206 g, 0.78 mmol) were dissolved in tetrahydrofuran (70 mL) and stirred at 25 °C. [PPN]CN (ca. 5 mg) was dissolved in the minimum amount of dichloromethane (ca. 0.5 mL), and added with a syringe. The initially orange solution immediately turned red, while gas evolution could be detected. Monitoring by infrared spectroscopy in the ν_{CO} region revealed complex formation with 100% spectroscopic yields within 2 min. As soon as THF was removed under vacuum, traces of complex 2 were already detected in the NMR spectrum (vide infra). Ru₃(CO)₁₁(PPh₂py) (1): IR (ν_{CO}, cm⁻¹, cyclohexane) 2093 (w), 2041 (m), 1925 (s), 1992 (w); ³¹P{¹H} NMR (25 °C, CDCl₃) δ 37.42 (s, terminal phosphorus).

Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₃H₄N))(CO)₉ (2). During routine attempts to chromatograph complex (1) by using dichloromethane/hexane (1/3) as eluent, the unique red band moving through the silica gel column gradually turned yellow, indicating formation of a new species, which was almost quantitatively recovered and subsequently identified as 2. Traces of an unknown brown material were retained on the column.

Upon standing in THF solution under an inert atmosphere at 25 °C, complex 1 was slowly converted into 2 over a period of 48 h. At 40 °C, the transformation was complete within 2 h (yield, 90%). IR (ν_{CO}, cm⁻¹, hexane): 2060 (w), 2045 (vs), 2020 (s), 1992 (m), 1973 (m), 1955 (w). Anal. Calcd for C₂₇H₁₄N₁O₁₀P₂Ru₃: C, 38.31; H, 1.67; N, 1.65. Found: C, 38.74; H, 1.65; N, 1.59. NMR: ¹³C (–60 °C, CD₂Cl₂) δ 302.37 (1 C, d, acyl carbon); ³¹P{¹H} (25 °C, CDCl₃) δ 48.93 (s, phosphido).

Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₃H₄N))(CO)₈(PR₃) (3). **General Procedure.** Complex 2 (0.5 g, 0.59 mmol) and the appropriate phosphine (PPh₃, 0.155 g, 0.59 mmol; PPh₂H, 0.110 g, 0.59 mmol; PCy₂H, 0.117 g, 0.059 mmol) were dissolved in THF (40 mL) and stirred at 30 °C, for 90 min. The resulting orange solutions were evaporated to dryness, and the residues were recrystallized from acetone/ethanol (1/3) (yield, ca. 90%).

Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₃H₄N))(CO)₈(P(C₆H₅)₃) (3a). IR (ν_{CO}, cm⁻¹, CHCl₃): 2050 (s), 2020 (vs), 1985 (m br), 1960 (m br), 1940 (sh). Anal. Calcd for C₄₄H₂₉N₁O₉P₂Ru₃: C, 48.89; H, 2.70; N, 1.30; P, 5.73. Found: C, 50.15; H, 3.13; N, 1.26; P, 5.59. NMR: ¹³C (–60 °C, CD₂Cl₂) δ 302.6 (1 C, s, acyl carbon); ³¹P{¹H} (25 °C, CDCl₃) δ 49.53 (1 P, d, phosphido, J(P–P) = 17.6 Hz), 26.26 (1 P, d, terminal phosphorus).

Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₃H₄N))(CO)₈(P(C₆H₅)₂H) (3b). The complex exists as two isomers (vide infra). IR (ν_{CO}, cm⁻¹, CHCl₃): 2050 (s), 2020 (vs), 1988 (m br), 1950 (m br), 1940 (sh).

Table I. Crystal and Intensity Data for Compounds 2 and 3a

	2	3a
formula	C ₂₇ H ₁₄ O ₁₀ NPRu ₃	C ₄₇ H ₃₅ O ₁₀ NP ₂ Ru ₃
fw	846.48	1080.87
a, Å	10.431 (2)	10.650 (4)
b, Å	15.888 (5)	31.023 (4)
c, Å	17.821 (5)	13.061 (2)
β, deg		97.57 (2)
V, Å ³	2953	4263
Z	4	4
ρ _{calcd} , g cm ⁻³	1.91	1.68
space group	D _{2h} ⁻ -P2 ₁ 2 ₁ 2 ₁	C _{2h} ⁻ -P2 ₁ /n
cryst shape	9-sided, face {001}, {011}, {101̄}, {101}	8-sided, face {101}, {021̄}, {021}, {011}, {01̄1}, {110}, {110}
cryst vol, mm ³	0.024	0.041
t, °C	20	20
radiation	d	d
linear abs coeff, cm ⁻¹	15.39	11.57
transmission factors	0.57–0.74	0.72–0.85
receiving aperture, mm	4 × 4	4 × 4
take-off angle, deg	2.0	4.0
scan mode	ω/θ	ω/2θ
scan range, deg	0.85 below Kα ₁ to 0.85 above Kα ₂	0.90 below Kα ₁ to 0.90 above Kα ₂
2θ limit, deg	3–55	3–48
no. of unique data used	2757	5770
(F _o ² > 3σ(F _o ²))		
weighting scheme, ^a p	0.03	0.04
no. of variable params	379	383
R(on F _o for F _o ² > 3σ(F _o ²)) ^b	4.2	4.8
R _w (on F _o for F _o ² > 3σ(F _o ²)) ^c	4.8	8.7

^a Weighting scheme: 1/σ², where σ²(F) = σ² + (pF²). ^b R = ∑|F_o – |F_c||/∑|F_o|. ^c R_w = [∑w(|F_o|² – |F_c|²)/∑w|F_o|²]^{1/2}. ^d Graphite-monochromated Mo Kα, λ(Mo Kα₁) = 0.7093 Å.

Anal. Calcd for C₃₈H₂₅N₁O₉P₂Ru₃: C, 45.42; H, 2.51; N, 1.39; Found: C, 45.53; H, 2.67; N, 1.48. ¹³C NMR (–60 °C, CD₂Cl₂): δ 276.6 (1 C, s, acyl carbon). ³¹P{¹H} NMR (25 °C, CDCl₃) cis isomer, δ 49.82 (1 P, d, phosphido, J(P–P) = 17.7 Hz), 15.91 (1 P, d, terminal phosphorus); trans isomer, δ 52.34 (1 P, d, phosphido, J(P–P) = 233.9 Hz), 24.73 (1 P, d, terminal phosphorus). ³¹P NMR (25 °C, CDCl₃): cis isomer, δ 49.8 (1 P, s (br), phosphido), 15.9 (1 P, d (br), terminal phosphorus, J(P–H) = 352 Hz); trans isomer, δ 52.3 (1 P, d (br), phosphido, J(P–P) = 234 Hz), 24.7 (1 P, d (br)–d (b), terminal phosphorus, J(P–H) = 344 Hz). Integration of ³¹P signals gives a cis/trans ratio of 10.

Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₃H₄N))(CO)₈(P(C₆H₁₁)₂H) (3c). The complex exists as two isomers. IR (ν_{CO}, cm⁻¹, CHCl₃) 2047 (s), 2015 (vs), 1980 (m br), 1955 (m br), 1920 (sh). Anal. Calcd for D₃₈H₃₇N₁O₉P₂Ru₃: C, 44.88; H, 3.67; N, 1.38; P, 6.09; Found: C, 44.90; H, 3.62; N, 1.36; P, 6.41. ³¹P{¹H} NMR (25 °C, CDCl₃): cis isomer, δ 49.45 (1 P, d, phosphido, J(P–P) = 16.2 Hz), 26.75 (1 P, d, terminal phosphorus); trans isomer, δ 51.47 (1 P, d, phosphido, J(P–P) = 220.0 Hz), 35.61 (1 P, d, terminal phosphorus). ³¹P NMR (25 °C, CDCl₃): cis isomer, δ 49.5 (1 P, s (br), phosphido), 26.8 (1 P, d (b), terminal phosphorus, J(P–H) = 332 Hz); trans isomer, δ 51.5 (1 P, d (br), phosphido, J(P–P) = 220 Hz), 35.6 (1 P, d (br)–d (br), terminal phosphorus, J(P–H) = 319 Hz). Integration of ³¹P signals gives a cis/trans ratio of 5.

Crystal Data Collection and Reduction. Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₃H₄N))(CO)₉ (2). Crystals of 2 were grown from dichloromethane/hexane (1/5) at –30 °C. The complex crystallizes in the orthorhombic system, space group D_{2h}⁻-P2₁2₁2₁. No attempt was made to determine the absolute configuration. Intensity data were recorded on an Enraf Nonius CAD4 diffractometer at 20 °C. The setting angles of 25 reflections with 12° < 2θ < 14° were refined by least-squares procedures and led to the cell constants. Crystal and intensity data are summarized in Table I. Intensities were corrected for Lorentz and polarization effects as well as absorption and reduced to structure factor amplitudes.

Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₃H₄N))(CO)₈(P(C₆H₅)₃) (3a). Crystals of 3 were grown from acetone/ethanol (1/5) at –30 °C. The complex crystallizes in the monoclinic system, space group C_{2h}⁻.

(12) Lugan, N.; Lavigne, G.; Bonnet, J.-J. *Inorg. Chem.* **1986**, *25*, 7.

(13) Mantovani, A.; Cenini, S. *Inorg. Chem.* **1986**, *25*, 7.

(14) Martinsen, A.; Songstad, S. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 645.

Table II. Positional Parameters and $B(\text{eq})$ for Compound 2

atom	x	y	z	$B(\text{eq}), \text{\AA}^2$
Ru(1)	0.21084 (8)	0.14080 (6)	0.11495 (5)	3.18 (2)
Ru(2)	0.46195 (8)	0.09108 (6)	0.07644 (5)	2.81 (1)
Ru(3)	0.23135 (8)	-0.01417 (6)	0.19762 (5)	3.01 (2)
P(1)	0.4232 (2)	0.0671 (2)	0.2049 (2)	2.68 (5)
C(1)	0.164 (1)	0.0723 (8)	0.0352 (8)	4.8 (3)
O(1)	0.135 (1)	0.0337 (6)	-0.0161 (6)	7.1 (3)
C(2)	0.036 (1)	0.1568 (8)	0.1481 (8)	4.8 (3)
O(2)	-0.0661 (9)	0.1680 (7)	0.1628 (7)	8.6 (3)
C(3)	0.234 (1)	0.2382 (7)	0.0546 (7)	4.3 (3)
O(3)	0.248 (1)	0.2944 (5)	0.0155 (6)	6.6 (2)
C(4)	0.5090 (9)	0.2024 (7)	0.0911 (6)	3.0 (2)
O(4)	0.5327 (8)	0.2717 (5)	0.0988 (5)	5.0 (2)
C(5)	0.434 (1)	0.1115 (8)	-0.0297 (7)	4.2 (3)
O(5)	0.425 (1)	0.1250 (7)	-0.0920 (5)	7.1 (3)
C(6)	0.639 (1)	0.0504 (7)	0.0684 (6)	3.8 (2)
O(6)	0.7393 (7)	0.0272 (6)	0.0619 (5)	5.7 (2)
C(7)	0.065 (1)	-0.0435 (8)	0.1605 (7)	4.5 (3)
O(7)	-0.0341 (9)	-0.0605 (6)	0.1397 (6)	7.2 (3)
C(8)	0.273 (1)	-0.1131 (8)	0.2554 (7)	4.7 (3)
O(8)	0.291 (1)	-0.1735 (6)	0.2867 (6)	7.1 (3)
C(9)	0.161 (1)	0.0482 (8)	0.2822 (7)	4.2 (3)
O(9)	0.1199 (9)	0.0860 (7)	0.3302 (5)	6.8 (2)
C(10)	0.3149 (9)	-0.0715 (6)	0.1032 (6)	3.1 (2)
O(10)	0.3987 (7)	-0.0336 (4)	0.0638 (4)	3.4 (2)
N(1)	0.2868 (9)	0.2065 (5)	0.2117 (5)	3.3 (2)
C(21)	0.383 (1)	0.1685 (7)	0.2487 (6)	2.9 (2)
C(22)	0.440 (1)	0.2053 (7)	0.3103 (7)	4.0 (3)
C(23)	0.397 (1)	0.2819 (8)	0.3343 (8)	5.2 (3)
C(24)	0.298 (1)	0.3215 (7)	0.2970 (8)	5.0 (3)
C(25)	0.244 (1)	0.2800 (7)	0.2371 (7)	4.3 (3)
C(11)	0.5570 (9)	0.0325 (7)	0.2646 (6)	2.9 (2)
C(12)	0.537 (1)	-0.0165 (7)	0.3268 (6)	3.7 (2)
C(13)	0.637 (1)	-0.0402 (7)	0.3736 (7)	4.6 (3)
C(14)	0.758 (1)	-0.0154 (9)	0.3567 (7)	5.0 (3)
C(15)	0.779 (1)	0.0336 (9)	0.2943 (7)	5.2 (3)
C(16)	0.683 (1)	0.0587 (8)	0.2486 (6)	3.8 (3)
C(31)	0.294 (1)	-0.1590 (7)	0.0749 (7)	3.6 (2)
C(32)	0.357 (2)	-0.1883 (9)	0.0149 (8)	6.2 (4)
C(33)	0.345 (2)	-0.271 (1)	-0.010 (1)	8.7 (5)
C(34)	0.260 (2)	-0.3214 (8)	0.0214 (9)	7.1 (4)
C(35)	0.192 (2)	-0.2947 (8)	0.080 (1)	7.4 (4)
C(36)	0.203 (1)	-0.2128 (6)	0.1082 (8)	4.9 (3)

^aValues for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

$P2_1/n$. Intensity data were recorded at 20 °C by using the above mentioned procedure. Crystal and intensity data are summarized in Table I. Intensities were corrected for absorption and reduced to structure factor amplitudes.

Solution and Refinement of the Structures. $\text{Ru}_3(\mu\text{-}\eta^2\text{-C(O)(C}_6\text{H}_5))(\mu_3\text{-}\eta^2\text{-P(C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{N}))(\text{CO})_9$ (2). The structure was solved, refined and analyzed by using the SDP crystallographic computing package.¹⁵ Atomic scattering factors were taken from Cromer and Waber's tabulations,¹⁶ anomalous dispersion corrections¹⁷ being applied to the Ru and P atoms. Direct methods allowed the location of Ru and P atoms; other non-hydrogen atoms were located by the usual combination of least-squares refinements and difference electron density techniques. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were entered in idealized positions and held fixed during refinements (C-H = 0.95 Å, B taken 1 Å² greater than the equivalent B of the atom to which it is attached). The final cycle of least-squares on F_o involving 379 variables for 2757 unique data with $F_o^2 > 3\sigma(F_o^2)$ led to $R(F) = 0.042$ and $R_w(F) = 0.048$. Final positional and equivalent isotropic thermal parameters for all non-hydrogen atoms are listed in Table II. Anisotropic thermal parameters (Table S1), and a

Table III. Positional Parameters and $B(\text{eq})$ for Compound 3a

atom	x	y	z	$B(\text{eq}), \text{\AA}^2$
Ru(1)	0.20128 (5)	0.27621 (2)	0.38441 (4)	2.30 (1)
Ru(2)	0.22956 (5)	0.33312 (2)	0.21795 (4)	2.20 (1)
Ru(3)	0.24102 (5)	0.35648 (2)	0.49555 (4)	2.46 (1)
P(1)	0.1040 (2)	0.36489 (6)	0.3348 (1)	2.34 (4)
P(2)	0.2615 (2)	0.38789 (7)	0.0932 (1)	2.64 (4)
C(1)	0.3769 (7)	0.2718 (3)	0.3969 (6)	3.1 (2)
O(1)	0.4846 (5)	0.2661 (2)	0.4050 (5)	4.5 (1)
C(2)	0.1895 (7)	0.2482 (3)	0.5155 (6)	3.5 (2)
O(2)	0.1885 (7)	0.2300 (2)	0.5917 (5)	5.3 (2)
C(3)	0.1845 (7)	0.2292 (3)	0.2881 (6)	3.2 (2)
O(3)	0.1864 (6)	0.2012 (2)	0.2330 (5)	5.2 (2)
C(4)	0.0865 (7)	0.3088 (3)	0.1451 (5)	3.1 (2)
O(4)	-0.0054 (6)	0.2949 (2)	0.1040 (5)	5.1 (1)
C(5)	0.3363 (7)	0.2919 (3)	0.1606 (6)	3.2 (2)
O(5)	0.3961 (7)	0.2663 (2)	0.1274 (6)	6.3 (2)
C(7)	0.3418 (7)	0.3245 (3)	0.6026 (6)	3.7 (2)
O(7)	0.3923 (6)	0.3048 (3)	0.6689 (5)	6.1 (2)
C(8)	0.2704 (8)	0.4124 (3)	0.5547 (7)	4.3 (2)
O(8)	0.2910 (8)	0.4450 (3)	0.5926 (7)	7.7 (2)
C(9)	0.0900 (7)	0.3430 (3)	0.5602 (6)	3.6 (2)
O(9)	0.0026 (6)	0.3347 (3)	0.5973 (5)	6.6 (2)
C(10)	0.3924 (7)	0.3671 (2)	0.4106 (5)	2.5 (1)
O(10)	0.3863 (4)	0.3607 (2)	0.3136 (4)	2.7 (1)
N(1)	0.0003 (5)	0.2889 (2)	0.3628 (4)	2.6 (1)
C(21)	-0.0350 (6)	0.3302 (3)	0.3425 (5)	2.6 (1)
C(22)	-0.1630 (7)	0.3424 (3)	0.3305 (6)	3.4 (2)
C(23)	-0.2548 (7)	0.3112 (3)	0.3384 (7)	4.1 (2)
C(24)	-0.2171 (7)	0.2691 (3)	0.3581 (7)	4.1 (2)
C(25)	-0.0887 (7)	0.2591 (3)	0.3713 (6)	3.4 (2)
C(11)	0.0192 (7)	0.4165 (3)	0.3020 (6)	3.0 (1)*
C(12)	-0.0461 (8)	0.4219 (3)	0.2046 (7)	3.3 (2)*
C(13)	-0.113 (1)	0.4603 (4)	0.1784 (8)	5.5 (2)*
C(14)	-0.109 (1)	0.4928 (4)	0.2515 (8)	5.4 (2)*
C(15)	-0.044 (1)	0.4879 (4)	0.3462 (8)	5.2 (2)*
C(16)	0.0201 (8)	0.4496 (3)	0.3741 (6)	3.7 (2)*
C(31)	0.5165 (7)	0.3863 (3)	0.4533 (6)	3.0 (1)*
C(32)	0.5654 (9)	0.4207 (3)	0.4079 (7)	4.7 (2)*
C(33)	0.682 (1)	0.4386 (4)	0.4469 (8)	5.4 (2)*
C(34)	0.752 (1)	0.4197 (4)	0.5313 (8)	5.7 (2)*
C(35)	0.711 (1)	0.3832 (4)	0.5748 (8)	5.4 (2)*
C(36)	0.592 (1)	0.3669 (3)	0.5388 (8)	4.3 (2)*
C(41)	0.2973 (7)	0.4436 (3)	0.1330 (6)	3.2 (1)*
C(42)	0.3411 (8)	0.4735 (3)	0.0677 (7)	3.9 (2)*
C(43)	0.3756 (9)	0.5139 (3)	0.1019 (8)	5.0 (2)*
C(44)	0.366 (1)	0.5267 (4)	0.2014 (8)	5.1 (2)*
C(45)	0.3233 (8)	0.4977 (3)	0.2681 (7)	4.1 (2)*
C(46)	0.2886 (8)	0.4568 (3)	0.2363 (6)	3.5 (2)*
C(51)	0.4030 (8)	0.3777 (3)	0.0288 (6)	3.6 (2)*
C(52)	0.4038 (9)	0.3739 (3)	-0.0771 (7)	4.2 (2)*
C(53)	0.519 (1)	0.3666 (4)	-0.1173 (8)	5.4 (2)*
C(54)	0.627 (1)	0.3645 (3)	-0.0524 (8)	5.1 (2)*
C(55)	0.6285 (9)	0.3677 (3)	0.0528 (7)	4.7 (2)*
C(56)	0.5179 (8)	0.3745 (3)	0.0931 (7)	3.9 (2)*
C(61)	0.1323 (8)	0.3932 (3)	-0.0137 (7)	3.7 (2)*
C(62)	0.0641 (9)	0.4317 (3)	-0.0324 (7)	4.7 (2)*
C(63)	-0.041 (1)	0.4337 (4)	-0.1099 (9)	6.0 (2)*
C(64)	-0.073 (1)	0.3977 (4)	-0.1645 (9)	6.1 (2)*
C(65)	-0.014 (1)	0.3608 (4)	-0.1535 (9)	6.3 (3)*
C(66)	0.0947 (9)	0.3571 (3)	-0.0701 (7)	4.7 (2)*

^aValues marked with an asterisk denote isotropically refined atoms. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

complete listing of observed and calculated structure factor amplitudes (Table S2) are available as supplementary material.

$\text{Ru}_3(\mu\text{-}\eta^2\text{-C(O)(C}_6\text{H}_5))(\mu_3\text{-}\eta^2\text{-P(C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{N}))(\text{CO})_9(\text{P(C}_6\text{H}_5)_3)$ (3a). The structure was solved, refined, and analyzed in the same way as the previous one (vide supra). However, in account of an important number of carbon atoms in this structure, we had to refine carbons of phenyl rings with isotropic thermal parameters in order to reduce the number of variable parameters. Although this approximation is reasonable, it affects the difference in R and R_w values (vide infra). The final cycle of least-squares refinement on F_o involving 383 variables for 5770 unique data with $F_o^2 > 3\sigma(F_o^2)$ led to $R(F) = 0.049$ and $R_w(F) =$

- (15) *Enraf-Nonius Structure Determination Package*, 4th ed.; B. A. Frenz & Associates, Inc.: College Station, TX; Enraf-Nonius: Delft, The Netherlands; 1981. Programs were implemented on a VAX 11/730 computer.
- (16) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.
- (17) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table IV. Interatomic Distances (Å) for Compounds 2 and 3a

	2	3a		2	3a
Ru(1)–Ru(2)	2.821 (1)	2.842 (1)	Ru(3)–C(10)	2.102 (9)	2.098 (4)
Ru(1)–Ru(3)	2.877 (1)	2.883 (1)	P(1)–C(11)	1.839 (7)	1.860 (4)
Ru(2)···Ru(3)	3.639 (1)	3.671 (1)	P(1)–C(21)	1.840 (10)	1.843 (4)
Ru(1)–N(1)	2.165 (8)	2.158 (1)	P(2)–C(41)		1.831 (4)
Ru(1)–C(1)	1.856 (9)	1.861 (4)	P(2)–C(51)		1.846 (4)
Ru(1)–C(2)	1.933 (11)	1.934 (5)	P(2)–C(61)		1.831 (5)
Ru(1)–C(3)	1.900 (11)	1.917 (5)	O(10)–C(10)	1.272 (10)	1.271 (4)
Ru(2)–P(1)	2.356 (2)	2.369 (1)	N(1)–C(21)	1.341 (11)	1.351 (5)
Ru(2)–P(2)		2.405 (1)	C(10)–C(31)	1.495 (11)	1.488 (5)
Ru(2)–O(10)	2.100 (6)	2.127 (2)	C(21)–C(22)	1.382 (13)	1.404 (5)
Ru(2)–C(4)	1.853 (10)	1.846 (4)	C(22)–C(23)	1.365 (16)	1.390 (6)
Ru(2)–C(5)	1.941 (10)	1.927 (4)	C(23)–C(24)	1.384 (14)	1.379 (7)
Ru(2)–C(6)	1.959 (10)		C(24)–C(25)	1.374 (13)	1.391 (6)
Ru(3)–P(1)	2.385 (2)	2.402 (1)	C(25)–N(1)	1.328 (13)	1.340 (5)
Ru(3)–C(7)	1.915 (10)	1.919 (5)	(C–O) ^a	1.13 (1)	1.14 (1)
Ru(3)–C(8)	1.927 (8)	1.906 (5)	(C–C) ^b	1.37 (3)	1.38 (3)
Ru(3)–C(9)	1.946 (10)	1.956 (4)			

^a Within carbonyl groups. ^b Within phenyl rings.

0.087. Final positional and equivalent isotropic thermal parameters for all non-hydrogen atoms are listed in Table III. Anisotropic thermal parameters (Table S3), and a complete listing of observed and calculated structure factor amplitudes (Table S4) are available as supplementary material.

Results

Syntheses. The monosubstitution of CO by diphenylpyridylphosphine into Ru₃(CO)₁₂ to give the complex Ru₃(CO)₁₁(PPh₂py) (1) proceeded quantitatively at ambient temperature within less than 2 min, by using trace amounts of either sodium benzophenone ketyl⁵ or [PPN]CN⁶ as catalysts. Complex 1 could not be isolated pure, due to its quantitative conversion into a new species 2 when it is run through the silica gel column. This transformation also occurred slowly in THF solution at 25 °C and could be accelerated upon heating at 40 °C. Complex 2 was subsequently identified as Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₅H₄N))(CO)₉. This new complex was found to experience high reactivity at ambient temperature, exemplified by its reaction with phosphines, to give Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₅H₄N))(CO)₈(L) (3) (3a, L = PPh₃; 3b, L = PPh₂H; 3c, L = PCy₂H).

Spectroscopic and Crystallographic Characterization of the Complexes. Ru₃(CO)₁₁(PPh₂py) (1) was unambiguously identified as the monosubstituted derivative by comparison of its infrared spectrum in the ν_{CO} region with relevant data for a series of mono- and disubstituted ruthenium complexes.⁵ Isolation of 1 as a pure material was hindered by the above-mentioned conversion into 2.

Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₅H₄N))(CO)₉ (2). The ³¹P spectrum for this complex showed a resonance at δ 48.93, consistent with the occurrence of a bridging phosphorus ligand spanning an open edge, with no metal–metal bond.¹⁸ Evidence for the presence of an acyl group was obtained from ¹³C data, showing a characteristic resonance at δ 302.37. Such features were confirmed by the solution of the X-ray structure. A perspective view of the complex is shown in Figure 1. Selected interatomic distances, and bond angles are listed in Tables IV and V, respectively. This 50-e cluster is an edge double-bridged species, involving a bridging acyl group C(O)(C₆H₅) and a bridging phenylpyridylphosphido group P(C₆H₅)(C₅H₄N), both spanning the open metal–metal vector (Ru(2)···Ru(3) = 3.639 (1) Å). Further coordination of the nitrogen atom of the pyridyl substituent on phosphorus to the unique ruthenium atom (Ru(1)–N(1) = 2.165 (8) Å) contributes to a stabilization of the trimetal core. The environment of each metal atom is achieved with three CO ligands, whose orientations are characteristic for edge double-bridged species; i.e., the carbonyls adjacent to the bridge are distributed in equatorial coordination sites (C(6)–O(6), C(8)–

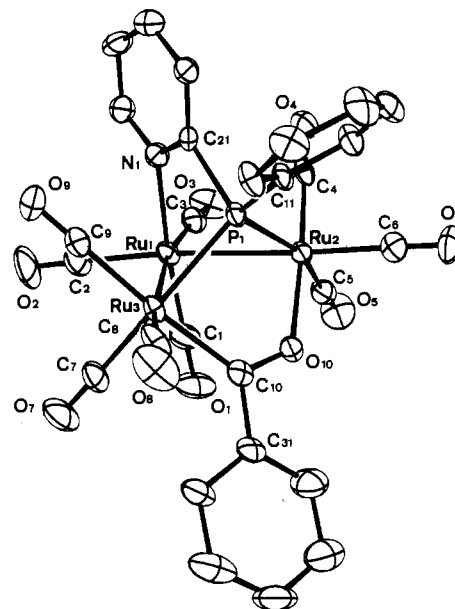


Figure 1. Perspective view of the complex Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₅H₄N))(CO)₉ (2).

O(8)), approximately trans to metal–metal vectors, and semiaxial sites (C(4)–O(4), C(5)–O(5), C(7)–O(7), C(9)–O(9)), trans to the atoms forming the double bridge.

Ru₃(μ-η²-C(O)(C₆H₅))(μ₃-η²-P(C₆H₅)(C₅H₄N))(CO)₈(L) (3) (3a, L = PPh₃; 3b, L = PPh₂H; 3c, L = PCy₂H). Spectroscopic data in solution for these substituted derivatives indicate retention of the geometry of the parent complex 2. In the case of PPh₃, (complex 3a) the additional phosphine ligand gives rise to a doublet in the ³¹P spectrum, with cis coupling constant *J*(P–P) = 16.2 Hz. For 3b and 3c, ³¹P NMR spectra reveal the existence of two isomers in which the phosphorus atoms are respectively cis and trans¹⁹ (3b: *J*(P–P)cis = 17.7 Hz, *J*(P–P)trans = 233.9 Hz. 3a: *J*(P–P)cis = 16.2 Hz, *J*(P–P)trans = 220.0 Hz). For compounds 3b and 3c, the isomers cis and trans are respectively in the ratio 10/1 and 5/1 (both cis and trans positions relative to the bridgehead phosphorus atom are cis relative to the oxygen of the acyl). The structure of complex 3a (Figure 2) shows that triphenyl phosphine occupies an equatorial coordination site on Ru(2), trans to Ru(1) and cis to both the phosphido ligand and the oxygen atom of the acyl group. Interatomic distances and bond angles within this structure (Tables IV and V) are closely related to those found for the unsubstituted parent complex 2, showing no significant

(18) (a) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* 1981, 204, C27. (b) Garrou, P. E. *Chem. Rev.* 1981, 81, 229.

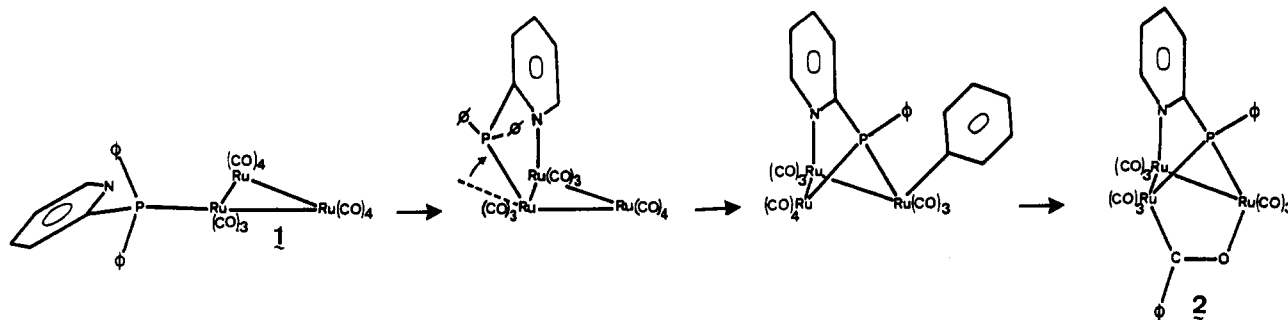
(19) Pregosin, A. S.; King, R. W. *³¹P and ¹³C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979.

Table V. Bond Angles (deg) for Compounds 2 and 3a

	2	3a		2	3a
Ru(2)-Ru(1)-Ru(3)	79.39 (3)	79.78 (1)	C(7)-Ru(3)-C(8)	100.9 (2)	97.5 (2)
Ru(2)-Ru(1)-N(1)	89.4 (2)	89.43 (9)	C(7)-Ru(3)-C(9)	93.0 (4)	89.4 (2)
Ru(2)-Ru(1)-C(1)	84.0 (3)	84.6 (1)	C(7)-Ru(3)-C(10)	89.6 (4)	93.9 (2)
Ru(2)-Ru(1)-C(2)	170.7 (3)	167.9 (1)	C(8)-Ru(3)-C(9)	94.9 (4)	97.0 (2)
Ru(2)-Ru(1)-C(3)	88.4 (3)	89.1 (1)	C(8)-Ru(3)-C(10)	89.0 (4)	88.5 (2)
N(1)-Ru(1)-C(1)	171.5 (4)	173.2 (2)	C(9)-Ru(3)-C(10)	174.9 (4)	173.2 (2)
N(1)-Ru(1)-C(2)	92.2 (4)	91.1 (2)	Ru(2)-P(1)-Ru(3)	100.30 (8)	100.62 (4)
N(1)-Ru(1)-C(3)	90.7 (4)	92.8 (1)	Ru(2)-P(1)-C(11)	118.7 (3)	120.6 (1)
C(1)-Ru(1)-C(2)	93.5 (4)	94.1 (2)	Ru(2)-P(1)-C(21)	108.0 (3)	108.5 (1)
C(1)-Ru(1)-C(3)	94.4 (5)	90.4 (2)	Ru(3)-P(1)-C(21)	107.7 (3)	106.8 (1)
C(2)-Ru(1)-C(3)	100.7 (4)	102.9 (2)	C(11)-P(1)-C(21)	120.5 (4)	121.0 (1)
Ru(1)-Ru(2)-P(1)	69.49 (5)	69.11 (3)	Ru(2)-P(2)-C(41)	101.0 (3)	98.4 (2)
Ru(1)-Ru(2)-P(2)		172.91 (3)	Ru(2)-P(2)-C(51)		121.2 (1)
Ru(1)-Ru(2)-O(10)	89.9 (2)	87.57 (7)	Ru(2)-P(2)-C(61)		112.5 (2)
Ru(1)-Ru(2)-C(4)	86.8 (3)	88.6 (2)	C(41)-P(2)-C(51)		97.9 (2)
Ru(1)-Ru(2)-C(5)	93.0 (3)	90.6 (2)	C(41)-P(2)-C(61)		103.8 (2)
Ru(1)-Ru(2)-C(6)	169.8 (4)		C(51)-P(2)-C(61)		104.3 (2)
P(1)-Ru(2)-P(2)		106.36 (4)	Ru(2)-O(10)-C(10)	127.1 (4)	125.3 (2)
P(1)-Ru(2)-O(10)	84.1 (2)	85.55 (8)	Ru(1)-N(1)-C(21)	116.6 (3)	116.4 (2)
P(1)-Ru(2)-C(4)	93.6 (3)	90.1 (1)	Ru(1)-N(1)-C(25)	125.0 (4)	124.3 (3)
P(1)-Ru(2)-C(5)	161.6 (3)	159.6 (1)	C(21)-N(1)-C(25)	118.5 (8)	119.3 (3)
P(1)-Ru(2)-C(6)	100.4 (3)		Ru(3)-C(10)-O(10)	121.5 (5)	123.8 (3)
P(1)-Ru(2)-P(2)		106.36 (4)	Ru(3)-C(10)-C(31)	127.7 (5)	124.9 (3)
P(2)-Ru(2)-C(4)		97.0 (1)	O(10)-C(10)-C(31)	110.8 (8)	111.1 (3)
C(4)-Ru(2)-C(5)	91.0 (5)		P(1)-C(11)-C(12)	121.5 (6)	119.2 (3)
C(4)-Ru(2)-C(6)	94.3 (4)		P(1)-C(11)-C(16)	120.1 (6)	121.4 (3)
C(5)-Ru(2)-C(6)	97.1 (4)		P(1)-C(21)-N(1)	110.9 (6)	111.0 (3)
C(5)-Ru(2)-P(2)		93.7 (1)	N(1)-C(21)-C(22)	121.7 (9)	121.3 (4)
Ru(1)-Ru(3)-P(1)	68.11 (6)	67.96 (3)	C(21)-C(22)-C(23)	118.9 (8)	119.0 (4)
Ru(1)-Ru(3)-C(7)	87.9 (3)	87.1 (1)	C(22)-C(23)-C(24)	120.1 (9)	118.9 (4)
Ru(1)-Ru(3)-C(8)	171.1 (2)	173.6 (1)	C(24)-C(25)-N(1)	123.5 (9)	122.0 (4)
Ru(1)-Ru(3)-C(9)	86.2 (3)	87.5 (1)	(Ru-C-O) ^a	177 (1)	176 (2)
Ru(1)-Ru(3)-C(10)	89.5 (2)	86.8 (1)	(C-C-C) ^b	120 (2)	120 (2)
P(1)-Ru(3)-C(7)	155.6 (3)	155.0 (2)			
P(1)-Ru(3)-C(8)	103.0 (2)	107.5 (2)			
P(1)-Ru(3)-C(9)	89.8 (3)	87.6 (1)			
P(1)-Ru(3)-C(10)	86.0 (2)	86.84 (1)			

^a Within carbonyl groups. ^b Within phenyl rings.

Scheme I



disturbance due to the incoming ligand.

Discussion

The isolation of the monosubstituted complex $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{py})$ (**1**) bears evidence that the catalysts have selectively promoted coordination of the phosphorus donor atom, while coordination of the nitrogen atom of the pyridyl group is not catalyzed. The spontaneous conversion of **1** into the acyl complex $\text{Ru}_3(\mu\text{-}\eta^2\text{-C(O)(C}_6\text{H}_5))(\mu_3\text{-}\eta^2\text{-P(C}_6\text{H}_5)(\text{C}_5\text{H}_4\text{N))}(\text{CO})_9$ (**2**) is a rather surprising feature. A first sight, there is no clear reason why an intermediate complex $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-PPh}_2\text{py})$ cannot be isolated. However, we note that nitrogen ligands shows a general tendency to coordinate at axial sites of trimetal clusters.²⁰

If this were to happen in $\text{Ru}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-PPh}_2\text{py})$, it would force the phosphorus atom into an axial position (Scheme I), known to be highly favorable for direct P-C bond cleavage at two metal centers.⁹ Such an explanation would account for the very mild conditions at which the cleavage of the P-C bonds is made to occur here, as compared with relevant examples in the literature.²¹

A further interesting feature is the formation of the acyl group. Though rarely observed,²²⁻²⁴ a σ -bonded aryl group may be reasonably involved at intermediate step. In many cases, subsequent reductive elimination of benzene is favored, assuming a hydride

(20) (a) Cotton, F. A.; Hanson, B. E.; Jamerson, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 6588. (b) Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2091. (c) Eisenstadt, A.; Giandomenico, C. M.; Frederick, M. F.; Laine, R. M. *Organometallics* **1985**, *4*, 2033.

(21) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

(22) Harding, M. M.; Nicholls, B. S.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1479.

(23) Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *Organometallics* **1985**, *4*, 935.

(24) Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 767.

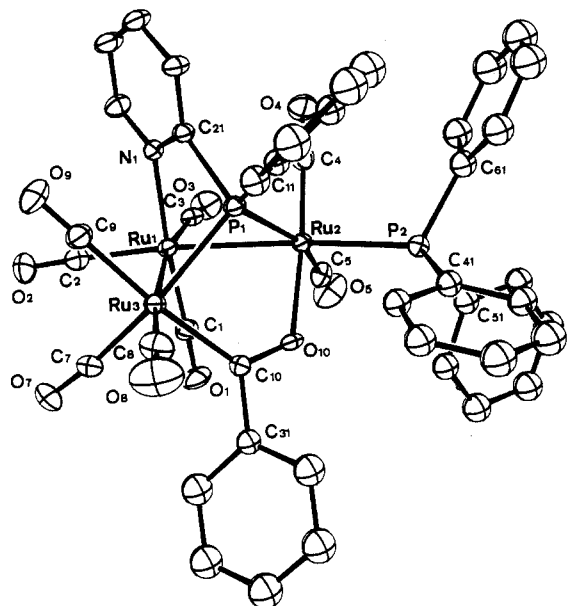


Figure 2. Perspective view of the complex $\text{Ru}_3(\mu\text{-}\eta^2\text{-C(O)(C}_6\text{H}_5))(\mu_3\text{-}\eta^2\text{-P(C}_6\text{H}_5)(\text{C}_5\text{H}_4\text{N))}(\text{CO})_8(\text{P(C}_6\text{H}_5)_3)$ (**3a**).

ligand is available.^{9,25} In the absence of any hydride here, the phenyl group undergoes migratory CO insertion to give the acyl group $\text{C(O)(C}_6\text{H}_5)$, as observed in few cases.^{26,27}

The new complex $\text{Ru}_3(\mu\text{-}\eta^2\text{-C(O)(C}_6\text{H}_5))(\mu_3\text{-}\eta^2\text{-P(C}_6\text{H}_5)(\text{C}_5\text{H}_4\text{N))}(\text{CO})_9$ (**2**) belongs to the family of reactive edge double-bridged species $\text{Ru}_3(\mu\text{-X})(\mu\text{-}\eta^2\text{-C(O)R)}(\text{CO})_{10}$ ($\text{X} = \text{H}$,

(25) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Organometallics* **1982**, *1*, 1040.

(26) (a) Blickensderfer, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2681. (b) Blickensderfer, J. R.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2686.

(27) Doel, G. R.; Feasey, N. D.; Knox, S. A. R.; Orpen, A. G.; Webster, J. *J. Chem. Soc., Chem. Commun.* **1986**, 542.

or halogens).^{28,29} Interestingly the presence of a face-capping group prevents the facile expulsion of the central metal atom,²⁹ without affecting the reactivity of the complex. Typically, in the presence of various phosphine ligands, we have observed stereospecific substitutions under ambient conditions to give the complexes $\text{Ru}_3(\mu\text{-}\eta^2\text{-C(O)(C}_6\text{H}_5))(\mu_3\text{-}\eta^2\text{-P(C}_6\text{H}_5)(\text{C}_5\text{H}_4\text{N))}(\text{CO})_8(\text{L})$ (**3**) (**3a**, $\text{L} = \text{PPh}_3$; **3b**, $\text{L} = \text{PPh}_2\text{H}$; **3c**, $\text{L} = \text{PCy}_2\text{H}$). In all cases, the incoming ligand occupies a site in a cis position relative to the oxygen of the acyl group. The complexes reported here offer a good opportunity to study one fundamental process in cluster chemistry, which is the reductive elimination of an organic group. This is the topic of our forthcoming paper.³⁰

Summary

The present study shows that oxidative cleavage of a P-C bond from diphenylpyridylphosphine, and subsequent migration of the resulting phenyl substituent to coordinated CO can be achieved at three ruthenium centers under mild conditions, even though the precursor complex is electronically saturated. The readily available acyl complex generated in this reaction possesses a metal framework stabilized by the face-bridging phenylpyridylphosphido group. Stereospecific substitution of one CO by a variety of phosphine ligands is seen to occur under ambient conditions at a cis position relative to the oxygen of the acyl group.

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Supplementary Material Available: Refined anisotropic thermal parameters for **2** and **3a** (Tables S1 and S3) (2 pages); calculated and observed structure factors for **2** and **3a** (Tables S2 and S4) (49 pages). Ordering information is given on any current masthead page.

(28) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4640.

(29) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4646.

(30) Lugan, N.; Lavigne, G.; Bonnet, J.-J., submitted for publication.

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N,N'-Di-*p*-tolylformamidinato-Bridged Mixed-Valence Iridium(I)-Iridium(III) Dimers Containing a Metal-Metal Dative Bond. Synthesis, Molecular Structure, and Physicochemical Properties

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The reaction between $[\text{Ir}(\mu\text{-form})(\text{COD})]_2$ (form = *N,N'*-di-*p*-tolylformamidinato ion; COD = 1,5-cyclooctadiene) and 2 equiv of AgOCOCF_3 produces $(\text{COD})\text{Ir}(\mu\text{-form})_2\text{Ir}(\text{OCOCF}_3)_2(\text{H}_2\text{O})$ (**1**), containing an unprecedented Ir(I)→Ir(III) dative bond. It also contains two monodentate trifluoroacetate groups coordinated to the Ir(III) atom. The compound has been characterized by IR and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{13}\text{C}\{\text{APT}\}$ NMR spectra (APT = attached proton test) and by elemental analyses. Interaction between **1** and a number of donor ligands has been investigated by ^1H NMR spectroscopy; the donor ligand replaces the H_2O molecule to afford similar mixed-valence compounds. The compound containing pyridine, $(\text{COD})\text{Ir}(\mu\text{-form})_2\text{Ir}(\text{OCOCF}_3)_2(\text{py})$ (**2**), has been isolated and characterized by X-ray crystallography: monoclinic, space group $P2_1/c$, $a = 20.236$ (6) Å, $b = 10.151$ (3) Å, $c = 25.080$ (11) Å, $\beta = 96.02$ (3)°, $V = 5174$ (3) Å³, $Z = 4$, $R = 0.0449$, $R_w = 0.0582$ for 3796 data having $I > 3\sigma(I)$. A cyclic voltammetric study on compounds **1** and **2** is also reported.

Introduction

Rhodium(II) dimers containing four bidentate bridging ligands and a single metal-metal bond of $\sigma^2\pi^4\delta^2\delta^*\pi^*\pi^*$ electronic configuration are well-known and relatively easily accessible in a number of ways,¹ the most common one being the direct interaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with an alkali-metal salt of the desired bridging ligand in the presence of methanol, which is both the

solvent and the reducing agent of the reaction. In such a way, simple compounds such as $\text{Rh}_2(\text{OCOR})_4$ and $\text{Rh}_2(\text{xhp})_4$ (xhp = 6-substituted hydroxypyridinato ion) have been prepared. On the other hand, the analogous Ir(II) compounds have not yet been reported, although a number of Ir(II) dimers with different structures are known, e.g. $[\text{Ir}(\text{H})(\mu\text{-S-}t\text{-Bu})(\text{CO})(\text{P}(\text{OMe})_3)]_2$,² $\text{Ir}_2(\text{C}_{10}\text{H}_4\text{S}_4)\text{Br}_2(\text{CO})_2(\text{PPh}_3)_2$,³ $[\text{IrX}(\mu\text{-pz})(\text{COD})]_2$ ($\text{X} = \text{Cl},^4$

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(2) Bonnet, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940.