Synthesis and Characterization of $Rh(P(CH_3)_3)_2(CO)CH_3$ and $Rh(P(CH_3)_3)_2(CO)Ph$

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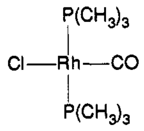
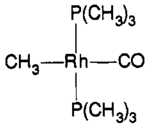
The new complexes $Rh(P(CH_3)_3)_2(CO)CH_3$ and $Rh(P(CH_3)_3)_2(CO)Ph$ were synthesized from $Rh(P(CH_3)_3)_2(CO)Cl$. The phenyl complex was synthesized by two routes, first by direct substitution of $Rh(P(CH_3)_3)_2(CO)Cl$ using diphenylmagnesium and second from the methyl derivative $Rh(P(CH_3)_3)_2(CO)CH_3$ by irradiation in the presence of benzene. $Rh(P(CH_3)_3)_2(CO)Ph$ reacts with HCl at low temperature to form the octahedral complex $Rh(P(CH_3)_3)_2(CO)(H)(Cl)Ph$, which is unstable for extended periods at temperatures above 250 K and eliminates benzene to give $Rh(P(CH_3)_3)_2(CO)Cl$ ($t_{1/2}$ = 12.3 min at 265 K). The structures of $Rh(P(CH_3)_3)_2(CO)Cl$, $Rh(P(CH_3)_3)_2(CO)CH_3$, and $Rh(P(CH_3)_3)_2(CO)Ph$ were determined by X-ray crystallography. All three complexes are square-planar. $Rh(P(CH_3)_3)_2(CO)CH_3$ has a $Rh-CH_3$ bond length of 2.130(9) Å, and $Rh(P(CH_3)_3)_2(CO)Ph$ has a Rh–C(phenyl) bond length of 2.096(4) Å. Crystals of $Rh(P(CH_3)_3)_2(CO)Cl$ are orthorhombic, space group *Pcab*, with a = 11.523(2) Å, b = 11.807(2) Å, c = 19.843(2) Å, V = 2699.7(6) Å^3, and Z = 8. Crystals of $Rh(P(CH_3)_3)_2(CO)CH_3$ are monoclinic, space group $P2_1/n$, with a = 9.944(5) Å, b = 10.136(3) Å, c = 13.266(6) Å, β = 94.06(4)°, V = 1334(1) Å^3, and Z = 4. Crystals of $Rh(P(CH_3)_3)_2(CO)Ph$ are monoclinic, space group $C2/c$, with a = 13.406(6) Å, b = 11.797(4) Å, c = 11.033(7) Å, β = 109.57(2)°, V = 1644(2) Å^3, and Z = 4.

Introduction

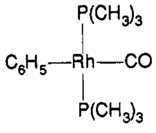
The photoactive complex *trans*-chlorocarbonylbis(trimethylphosphine)rhodium(I) (1) is one of the most efficient reagents for the catalytic activation and functionalization of hydrocarbons.[1] The complex reacts with both linear and branched alkanes to give organorhodium complexes which eventually form organic products, e.g. by carbonylation (under CO) or dehydrogenation. As part of an ongoing investigation of the reaction chemistry of $Rh(P(CH_3)_3)_2(CO)Cl$ and its derivatives, we have synthesized and crystallographically characterized two new organorhodium complexes, $Rh(P(CH_3)_3)_2(CO)CH_3$ (2) and $Rh(P(CH_3)_3)_2(CO)Ph$ (3). We also report here the crystal structure of the parent complex, 1.


$Cl-\overset{P(CH_3)_3}{\underset{P(CH_3)_3}{Rh}}-CO$

1


$CH_3-\overset{P(CH_3)_3}{\underset{P(CH_3)_3}{Rh}}-CO$

2


$C_6H_5-\overset{P(CH_3)_3}{\underset{P(CH_3)_3}{Rh}}-CO$

3

Experimental Section

General Data. All manipulations were carried out using standard Schlenk or vacuum line methods or in a drybox equipped with a continuous slow nitrogen purge. NMR spectra were obtained on a Bruker AMX400 spectrometer. ^{31}P NMR spectra (162 MHz) were referenced to external, neat trimethyl phosphite, taken as 140.85 ppm at the temperature quoted. ^1H NMR spectra (400.1 MHz) and ^{13}C NMR (100.6 MHz) spectra were referenced to residual solvent resonances. Infrared spectra were recorded on a Biorad FT S20/80 spectrometer. UV/visible spectra were recorded on a Hitachi 150-20 spectrophotometer. Nitrogen (>99.5%) and carbon monoxide (>99.5%) were purchased from CIG-HYTEC and used as obtained. Pentane, tetrahydrofuran, benzene, and diethyl ether were stored over sodium benzophenone ketyl under a dry nitrogen atmosphere and distilled immediately prior to use. THF-d_8 was obtained from Merck and used without further purification. $RhCl_3 \cdot 3H_2O$ was obtained from Johnson-Matthey. Trimethylphosphine was obtained from Aldrich Chemicals and used as obtained. $[RhCl(CO)_2]_2$,[2] dimethylmagnesium,[3] and diphenylmagnesium[3] were prepared using the published procedures.

Preparation of $Rh(P(CH_3)_3)_2(CO)Cl$ (1). $Rh(P(CH_3)_3)_2(CO)Cl$ was prepared by following the general procedure outlined by McCleverty and Wilkinson[2a] for the preparation of $Rh(PPh_3)_2(CO)Cl$ and Deeming and Shaw[2b] for the preparation of $Rh(P(CH_3)_3)_2(CO)Cl$. Trimethylphosphine (380 mg, 5.0 mmol) was added dropwise to a stirred solution of $[Rh(CO)_2Cl]_2$ (470 mg, 1.2 mmol) in benzene (20 mL). The solvent was removed under vacuum, and the crude product was purified by sublimation (80 °C, 0.0025 Torr). Slow evaporation of a saturated solution of the sublimate in diethyl ether afforded 1 as yellow prisms (620 mg, 81%), mp 181 °C (lit.[4] mp 181 °C). Crystals obtained by this procedure were suitable for X-ray diffraction analysis. $^{31}P\{^1H\}$ NMR (THF-d_8, 230 K): δ −10.03 ppm (d, $^1J_{Rh-P}$ = 114.7 Hz). ^1H NMR (THF-d_8, 230 K): δ 1.49 ppm (m, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 190.6 (dt, *C*O, $^1J_{Rh-C}$ = 74.8, $^2J_{C-P}$ = 16.8 Hz), 17.0 ppm (m, $P(CH_3)_3$). λ_{max} (diethyl ether) 359, 269 nm. ν_{CO} (Nujol): 1960 cm^{-1}.

Preparation of $Rh(P(CH_3)_3)_2(CO)CH_3$ (2). $Rh(P(CH_3)_3)_2(CO)CH_3$ was obtained by treatment of a solution of 1 (150 mg, 0.47 mmol) in THF (0.5 mL) with a solution of dimethylmagnesium in THF (0.36 mL, 0.65 M, 0.235 mmol) at −78 °C. The solution was transferred into pentane (10 mL, −78 °C) by cannula and centrifuged at low temperature (<−20 °C) and the super-

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(1) See for example: (*a*) Tanaka, M. *CHEMTECH* **1989**, 59. (*b*) Tanaka, M.; Sakakura, T. *Pure Appl. Chem.* **1990**, *62*, 1147. (*c*) Sakakura, T.; Sodeyama, T.; Tanaka, M. *Nouv. J. Chim.* **1989**, *13*, 737. (*d*) Sakakura, T.; Sodeyama, T.; Sasaki, K.; Wada, K.; Tanaka, M. *J. Am. Chem. Soc.* **1990**, *112*, 7221. (*e*) Nomura, K.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 161. (*f*) Maguire, J. A.; Boese, W. J.; Goldman, A. S. *J. Am. Chem. Soc.* **1989**, *111*, 7088.

(2) (*a*) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211. (*b*) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 597.

(3) Luhder, K.; Nehls, D.; Madeja, K. *J. Prakt. Chem.* **1983**, *325*, 1027.

(4) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hirsthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 511.

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natant separated from the precipitated magnesium salts. The solvent was removed under vacuum and the residue sublimed (40 °C, 0.0025 Torr). Slow evaporation of a saturated solution of the sublimate in pentane afforded **2** as deep yellow prisms (192 mg, 66%; mp 72–74 °C dec). Crystals obtained by this procedure were suitable for X-ray diffraction analysis. $^{31}P\{^1H\}$ NMR (THF-d_8, 230 K): δ −9.72 ppm (d, $^1J_{Rh-P}$ = 136.3 Hz). ^1H NMR (THF-d_8, 230 K): δ 1.42 (m, $P(CH_3)_3$), −0.74 ppm (td, $^3J_{P-H}$ = 9.2, $^2J_{Rh-H}$ = 1.6 Hz, $RhCH_3$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 192.6 (dt, CO, $^1J_{Rh-C}$ = 56.6, $^2J_{P-C}$ = 14.8 Hz), 16.5 (m, $P(CH_3)_3$), −2.7 ppm (dt, $^1J_{Rh-C}$ = 20.2, $^2J_{P-C}$ = 13.2 Hz, $RhCH_3$). λ_{max} (pentane): 392, 314 nm. ν_{CO} (pentane): 1948 cm^{-1}. Anal. Calcd for $C_8H_{21}P_2ORh$: C, 32.23; H, 7.10. Found: C, 31.9; H, 7.1.

Preparation of $Rh(P(CH_3)_3)_2(CO)C_6H_5$ (3). Irradiation of a solution of **2** (112 mg, 80 mM) in benzene/THF (1:3 v/v) with a 125-W medium-pressure mercury vapor lamp at −40 °C for 48 h resulted in quantitative formation of $Rh(P(CH_3)_3)_2(CO)C_6H_5$ (**3**). The solvent was removed under vacuum, and the residue was purified by sublimation (60 °C, 0.0025 Torr). Slow evaporation of a saturated solution of the sublimate in pentane afforded **3** as deep yellow prisms (10 mg, 68%; mp 82–84 °C dec). Crystals obtained by this procedure were suitable for X-ray diffraction analysis.

Alternatively, **3** was prepared by treatment of **1** with diphenylmagnesium. A solution of diphenylmagnesium in THF (0.436 mL, 0.55 M, 0.24 mmol) was added to a solution of $Rh(P(CH_3)_3)_2(CO)Cl$ (153 mg, 0.48 mmol) in THF (5 mL, −78 °C). The resulting golden yellow solution was transferred into pentane (10 mL, −78 °C) by cannula, centrifuged at low temperature (<−20 °C), and separated from the precipitated magnesium salts. The solvent was removed under vacuum and the residue sublimed (60 °C, 0.0025 Torr) to give **3** as a golden yellow solid (86 mg, 0.24 mmol, 50%). $^{31}P\{^1H\}$ NMR (THF-d_8, 230 K): δ −14.13 ppm (d, $^1J_{Rh-P}$ = 137.2 Hz). ^1H NMR (THF-d_8, 230 K): δ 7.28 (m, Ar $H_{A,A'}$), 6.98 (m, Ar $H_{M,M'}$), 6.83 (m, Ar H_X), 1.32 ppm (m, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR (THF-d_8, 230 K): δ 198.0 (dt, CO, $^1J_{Rh-C}$ = 55.4, $^2J_{P-C}$ = 14.0 Hz), 175.5 (dt, Ar C_{ipso}, $^1J_{Rh-C}$ = 26.6, $^2J_{P-C}$ = 16.8 Hz), 140.2 (t, Ar C_2, $^3J_{P-C}$ = 3.6 Hz), 127.7 (s, Ar C_3), 123.5 (s, Ar C_4), 17.8 ppm (m, $P(CH_3)_3$). λ_{max} (pentane): 401, 317 nm. ν_{CO} (pentane): 1959 cm^{-1}.

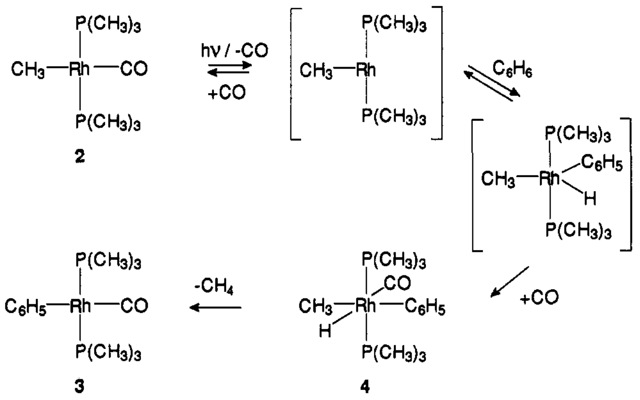
Reaction of 3 with HCl. A solution of hydrogen chloride in THF (40 μL, 0.79 M, 1.5 equiv), prepared by bubbling gaseous HCl through freshly distilled THF, was added via a gastight syringe to a solution of $Rh(P(CH_3)_3)_2(CO)C_6H_5$ (**3**) (8 mg, 22 μmol) in THF (0.5 mL, −40 °C). The mixture was briefly shaken to ensure homogeneity. The solution changed immediately from yellow to colorless. NMR spectroscopy (230 K) indicated that only one species, $Rh(P(CH_3)_3)_2(CO)(C_6H_5)(H)Cl$ (**5**), was present in the solution.[5] $Rh(P(CH_3)_3)_2(CO)(C_6H_5)(H)Cl$ (**5**): $^{31}P\{^1H\}$ NMR (THF-d_8, 230 K) δ −8.76 ppm (d, $^1J_{Rh-P}$ = 96.6 Hz); ^1H NMR (THF-d_8, 230 K): δ 8.18, 7.42 (2 × m, 2 × 1H, Ar H_{ortho}), 7.08–6.99 (3 × m, 3 × 1H, Ar $H_{meta,para}$), 1.42 (m, $P(CH_3)_3$), −14.78 ppm (dt, $^1J_{Rh-H}$ = 29.5, $^2J_{P-H}$ = 13.8 Hz, 1H, Rh–H).

Crystallographic Analyses. Cell constants were determined by least-squares fits to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. Data were reduced, and Lorentz, polarization, and absorption corrections were applied using the Enraf-Nonius structure determination package (SDP).[6] The structures were solved by heavy-atom methods using SHELX-76[7] and were refined by full-matrix least-squares analysis. Hydrogen atoms in **1** and **2** were included at calculated sites (C–H = 0.97 Å) with group thermal parameters, and those in **3** were refined with individual isotropic thermal parameters. All other atoms except minor contributors to disordered groups were refined anisotropically. Scattering factors and anomalous dispersion corrections for Rh were taken from ref 8, and for all others the values supplied in SHELX-76 were used. Crystal data for these analyses are provided in Table I.

Table I. Crystallographic Data for Diffraction Studies

	1	2	3
empirical formula	$C_7H_{18}ClP_2ORh$	$C_8H_{21}P_2ORh$	$C_{13}H_{23}P_2ORh$
mol wt	318.53	298.11	359.84
cryst syst	orthorhombic	monoclinic	monoclinic
lattice params			
a, Å	11.423(2)	9.944(5)	13.406(6)
b, Å	11.807(2)	10.136(3)	11.797(4)
c, Å	19.843(2)	13.266(6)	11.033(7)
α, deg	90.0	90.0	90.0
β, deg	90.0	94.06(4)	109.57(5)
γ, deg	90.0	90.0	90.0
V, Å^3	2676.2(6)	1334(1)	1644(2)
space group	*Pcab*	$P2_1/n$	$C2/c$
Z	8	4	4
D_{calc}, g/cm^3	1.581	1.485	1.485
$F(000)$	1280	608	736
μ(Mo Kα), cm^{-1}	14.51	14.28	11.65
temp, °C	21	21	21
range of hkl	0–13, 0–13, 0–23	−10 to +10, 0–10, 0–14	−15 to +15, 0–14, 0–13
$2\theta_{max}$, deg	1.0–50.0	1.0–45.0	1.0–50.0
no. of data with $I > 2.5\sigma(I)$	1933	1291	1194
no. of variables	116	116	127
residuals: R, R_w	0.024, 0.030	0.037, 0.042	0.024, 0.028
max shift in final cycle	0.001	0.002	0.007
max/min peaks	+0.4/−0.36	+0.84/−0.54	+0.23/−0.25
abs cor	analytical	analytical	analytical

Scheme I



Results and Discussion

$Rh(P(CH_3)_3)_2(CO)CH_3$ (**2**) was synthesized by treatment of $Rh(P(CH_3)_3)_2(CO)Cl$ (**1**) with dimethylmagnesium at low temperature. The arylrhodium complex $Rh(P(CH_3)_3)_2(CO)Ph$ (**3**) was formed quantitatively when **2** was irradiated in a solution of benzene in THF at low temperature. Although no intermediate compounds were detected in the conversion of **2** to **3**, the reaction possibly proceeds in a manner similar to that proposed for hydrocarbon activation[1] by $Rh(P(CH_3)_3)_2(CO)Cl$, i.e., photoinitiated loss of carbon monoxide to give $[Rh(P(CH_3)_3)_2CH_3]$, which adds oxidatively to benzene and regains CO to form $Rh(P(CH_3)_3)_2(CO)(Ph)(CH_3)H$ (**4**). A facile elimination of methane from **4** affords the observed product (Scheme I).

The phenylrhodium complex **3** was also formed by careful treatment of **1** with diphenylmagnesium. Syntheses of the related complexes $Rh(P(Ph)_3)_2(CO)CH_3$ and

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[5] Boyd, S. E. Ph.D. Thesis, The University of Sydney, 1992; manuscript in preparation.

[6] Enraf-Nonius Structure Determination Package (SDP); Enraf-Nonius: Delft, Holland, 1985.

[7] Sheldrick, G. M. *SHELX-76, a Program for X-Ray Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

[8] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

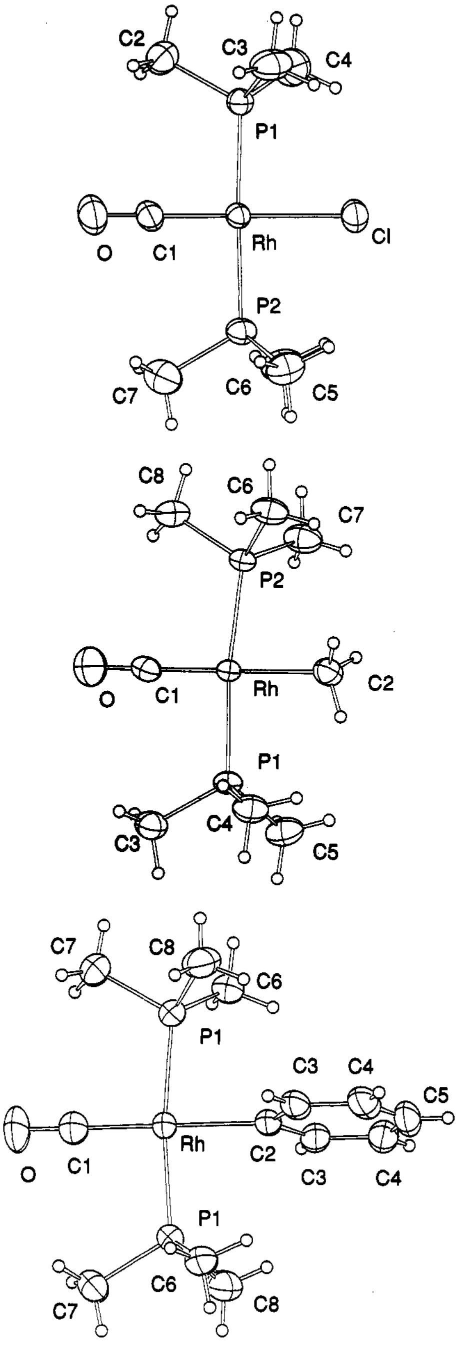

Figure 1. ORTEP plots of the complexes $Rh(P(CH_3)_3)_2(CO)Cl$ (**1**, top), $Rh(P(CH_3)_3)_2(CO)CH_3$ (**2**, middle), and $Rh(P(CH_3)_3)_2(CO)Ph$ (**3**, bottom). The numbering systems for the non-hydrogen atoms are shown.

Table II. Positional Parameters (×10⁴) for $Rh(P(CH_3)_3)_2(CO)Cl$ (1)

	x	*y*	*z*
Rh(1)	3104(1)	5334(1)	8734(1)
P(1)	3546(1)	4233(1)	7808(1)
P(2)	2758(1)	6457(1)	9666(1)
Cl(1)	4890(1)	6300(1)	8591(1)
C(1)	1754(3)	4621(3)	8841(2)
O(1)	892(3)	4136(3)	8905(2)
C(2)	2569(4)	3081(3)	7594(2)
C(3)	3587(5)	5007(3)	7029(2)
C(4)	4942(3)	3551(4)	7854(3)
C(5)	2799(4)	7959(3)	9502(2)
C(6)	3809(5)	6257(4)	10332(2)
C(7)	1378(4)	6286(4)	10107(2)

$Rh(P(Ph)_3)_2(CO)C_6H_5$ have been reported previously[9] using electrochemical methods. Both **2** and **3** are thermally unstable and decompose slowly on warming or on prolonged storage at ambient temperatures. Both **2** and **3** react with protic solvents and decompose within minutes on exposure to air.

In contrast to the photoinduced C–H activation chemistry exhibited by both the parent complex **1** and its methyl derivative **2**, $Rh(P(CH_3)_3)_2(CO)Ph$ (**3**) is significantly less reactive under photochemical conditions. Irradiation of **3** (100 mM) in a THF solution containing benzene-d_6 (benzene-d_6/THF-d_8, 1:3) under a nitrogen atmosphere showed <1% incorporation of C_6D_6 even after extended periods of irradiation (72 h, −40 °C).

Crystals of **1**–**3** suitable for X-ray crystallography were obtained by slow recrystallization from diethyl ether or pentane near ambient temperature. Figure 1 shows ORTEP plots of complexes **1**–**3**. Final atomic positional parameters for **1**–**3** are listed in Tables II, V, and VIII, respectively. Interatomic distances and angles are listed in Tables III, IV, VI, VII, IX, and X.

Complexes **2** and **3** are the first square-planar Rh(I) complexes with an alkyl or aryl carbon-to-metal bond to be characterized crystallographically. Both IR and X-ray diffraction data show a strengthening of the metal–carbonyl interaction in complex **2** (1.193(12) Å, ν_{CO} = 1948 cm^{-1}) relative to complexes **1** (1.146(4) Å, ν_{CO} = 1960 cm^{-1}) and **3** (1.140(7) Å, ν_{CO} = 1959 cm^{-1}). A decrease in the energy of ν_{CO} and a consequent lengthening in the C–O bond is not unexpected for a complex with a poor π-acid ligand, e.g. a methyl group, occupying a position trans to the carbonyl ligand. Complex **3**, however, while having an extended metal–carbonyl bond, more closely approximates the parent complex **1**, in both the carbonyl stretching frequency and the length of the C–O bond. The small difference observed in the length of the Rh–C(2) bond, when the CH_3– ligand is replaced by C_6H_5–, is of the order expected for the difference in the covalent radius of the sp^2- and sp^3-hybridized carbon atoms. The Rh–CH_3 bond length in **2** (2.130(9) Å) is slightly shorter than that reported for the Ir–CH_3 bond in $Ir(P(Ph)_3)_2(CO)CH_3$,[10] and the core bond lengths observed in **1**, Rh–P (2.307(1) Å), Rh–Cl (2.354(1) Å), and Rh–CO (1.770(4) Å) are almost identical with the corresponding distances reported[11] for $Rh(P(Ph)_3)_2(CO)Cl$ (2.322(1), 2.382(1), and 1.77(1) Å, respectively).

In the $^{13}C\{^1H\}$ NMR spectra of complexes **2** and **3** both the methyl and ipso aryl carbons exhibit the expected doublet of triplet splittings due to coupling to both ^{103}Rh and to ^{31}P in the two symmetrically disposed phosphine ligands. Triplet splittings due to ^{31}P coupling are also seen in the ^{13}C resonances of carbon atoms ortho to the rhodium metal on the aryl ligand of **3**. The protons of the methyl ligand of **2** resonate to high field of TMS in the ^1H NMR spectrum (δ −0.74 ppm), and the resonance appears as a well-resolved rhodium- and phosphorus-coupled triplet of doublets ($^3J_{P-H}$ = 9.2 Hz, $^2J_{Rh-H}$ = 1.6 Hz). No long-range heteronuclear coupling was resolved in the aryl region of the ^1H NMR spectrum of **3**. Complexes **2** and **3** both exhibit similar values for $^1J_{Rh-CO}$ (ca. 55 Hz) and also for $^1J_{Rh-P}$ (ca. 137 Hz), and these are significantly

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(9) (*a*) Zecchin, S.; Schiavon, G.; Pilloni, G.; Martelli, M. *J. Organomet. Chem.* **1976**, *110*, C45. (*b*) Schiavon, G.; Zecchin, S.; Pilloni, G.; Martelli, M. *J. Organomet. Chem.* **1976**, *120*, 261.

(10) Rees, W. M.; Churchill, M. R.; Li, T.-J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162.

(11) Dunbar, K. R.; Haefner, S. C. *Inorg. Chem.* **1992**, *31*, 3676.

Table III. Bond Lengths (Å) for $Rh(P(CH_3)_3)_2(CO)Cl$ (1)

P(1)–Rh(1)	2.307(1)	P(2)–Rh(1)	2.309(1)
Cl(1)–Rh(1)	2.354(1)	C(1)–Rh(1)	1.770(4)
C(2)–P(1)	1.810(4)	C(3)–P(1)	1.795(4)
C(4)–P(1)	1.789(4)	C(5)–P(2)	1.803(3)
C(6)–P(2)	1.801(4)	C(7)–P(2)	1.814(5)
O(1)–C(1)	1.146(4)		

Table IV. Bond Angles (deg) for $Rh(P(CH_3)_3)_2(CO)Cl$ (1)

P(2)–Rh(1)–P(1)	177.2(0)	Cl(1)–Rh(1)–P(1)	89.3(0)
Cl(1)–Rh(1)–P(2)	88.1(0)	C(1)–Rh(1)–P(1)	91.0(1)
C(1)–Rh(1)–P(2)	91.6(1)	C(1)–Rh(1)–Cl(1)	179.4(1)
C(2)–P(1)–Rh(1)	118.4(1)	C(3)–P(1)–Rh(1)	113.9(1)
C(3)–P(1)–C(2)	101.4(2)	C(4)–P(1)–Rh(1)	114.1(1)
C(4)–P(1)–C(2)	102.9(2)	C(4)–P(1)–C(3)	104.5(3)
C(5)–P(2)–Rh(1)	114.5(1)	C(6)–P(2)–Rh(1)	113.5(1)
C(6)–P(2)–C(5)	104.1(2)	C(7)–P(2)–Rh(1)	118.1(2)
C(7)–P(2)–C(5)	102.7(2)	C(7)–P(2)–C(6)	102.2(2)
O(1)–C(1)–Rh(1)	178.4(4)		

Table V. Positional Parameters (×10⁴) for $Rh(P(CH_3)_3)_2(CO)CH_3$ (2)

	x	*y*	*z*
Rh(1)	–43(1)	2217(1)	2285(1)
P(1)	1629(2)	3746(2)	2143(2)
P(2)	–1726(2)	665(2)	2226(2)
C(1)	140(8)	2196(8)	3617(9)
O(1)	242(9)	2175(9)	4518(7)
C(2)	–281(9)	2235(7)	676(7)
C(3)	2422(8)	4384(8)	3305(7)
C(4)	1154(8)	5225(7)	1452(7)
C(5)	3090(7)	3174(9)	1486(8)
C(6)	–3313(7)	1116(8)	1564(7)
C(7)	–1356(8)	–853(8)	1592(8)
C(8)	–2278(8)	72(8)	3416(7)

Table VI. Bond Lengths (Å) for $Rh(P(CH_3)_3)_2(CO)CH_3$ (2)

P(1)–Rh(1)	2.291(2)	P(2)–Rh(1)	2.294(2)
C(1)–Rh(1)	1.764(12)	C(2)–Rh(1)	2.130(9)
C(3)–P(1)	1.801(8)	C(4)–P(1)	1.803(7)
C(5)–P(1)	1.840(8)	C(6)–P(2)	1.809(7)
C(7)–P(2)	1.805(8)	C(8)–P(2)	1.810(8)
O(1)–C(1)	1.193(12)		

Table VII. Bond Angles (deg) for $Rh(P(CH_3)_3)_2(CO)CH_3$ (2)

P(2)–Rh(1)–P(1)	173.4(1)	C(1)–Rh(1)–P(1)	93.8(2)
C(1)–Rh(1)–P(2)	92.8(2)	C(2)–Rh(1)–P(1)	86.7(2)
C(2)–Rh(1)–P(2)	86.7(2)	C(2)–Rh(1)–C(1)	179.5(2)
C(3)–P(1)–Rh(1)	116.7(3)	C(4)–P(1)–Rh(1)	116.0(3)
C(4)–P(1)–C(3)	102.7(4)	C(5)–P(1)–Rh(1)	115.4(3)
C(5)–P(1)–C(3)	101.9(4)	C(5)–P(1)–C(4)	102.0(4)
C(6)–P(2)–Rh(1)	116.9(3)	C(7)–P(2)–Rh(1)	115.4(3)
C(7)–P(2)–C(6)	100.9(4)	C(8)–P(2)–Rh(1)	117.6(3)
C(8)–P(2)–C(6)	101.5(4)	C(8)–P(2)–C(7)	102.0(4)
O(1)–C(1)–Rh(1)	178.9(7)		

Table VIII. Positional Parameters (×10⁴) for $Rh(P(CH_3)_3)_2(CO)Ph$ (3)

	x	*y*	*z*
Rh(1)	5000	4845(1)	2500
C(1)	5000	6404(5)	2500
O(1)	5000	7370(3)	2500
C(2)	5000	3068(4)	2500
C(3)	4738(3)	2429(3)	3417(4)
C(4)	4747(3)	1255(4)	3418(6)
C(5)	5000	677(6)	2500
P(1)	3327(1)	4724(1)	1040(1)
C(6)	2371(3)	3983(4)	1583(5)
C(7)	2645(4)	6048(4)	446(6)
C(8)	3214(5)	4013(5)	–455(5)

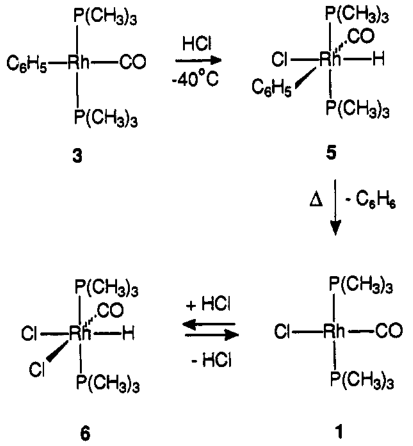
Table IX. Bond Lengths (Å) for $Rh(P(CH_3)_3)_2(CO)Ph$ (3)

C(1)–Rh(1)	1.839(5)	C(2)–Rh(1)	2.096(4)
P(1)–Rh(1)	2.286(1)	O(1)–C(1)	1.140(7)
C(3)–C(2)	1.397(4)	C(4)–C(3)	1.384(6)
C(5)–C(4)	1.356(6)	C(6)–P(1)	1.812(4)
C(7)–P(1)	1.815(4)	C(8)–P(1)	1.802(5)

Table X. Bond Angles (deg) for $Rh(P(CH_3)_3)_2(CO)Ph$ (3)

C(2)–Rh(1)–C(1)	180.0(0)	P(1)–Rh(1)–C(1)	93.6(0)
P(1)–Rh(1)–C(2)	86.4(0)	O(1)–C(1)–Rh(1)	180.0(0)
C(3)–C(2)–Rh(1)	122.7(2)	C(4)–C(3)–C(2)	122.4(5)
C(3)–C(2)–C(3)	114.7(5)	C(5)–C(4)–C(3)	120.4(6)
C(4)–C(5)–C(4)	119.5(6)	C(6)–P(1)–Rh(1)	115.6(1)
C(7)–P(1)–Rh(1)	117.1(2)	C(7)–P(1)–C(6)	101.8(2)
C(8)–P(1)–Rh(1)	115.7(2)	C(8)–P(1)–C(6)	102.9(3)
C(8)–P(1)–C(7)	101.5(2)	P(1)–Rh(1)–P(1)	172.9(0)

Scheme II



different from those in the parent complex 1 ($^1J_{\mathrm{Rh\text{-}CO}}$ = 74.8 Hz and $^1J_{\mathrm{P\text{-}Rh}}$ = 114.7 Hz).

Reaction of $Rh(P(CH_3)_3)_2(CO)C_6H_5$ with HCl. Treatment of 3 with a dilute solution of HCl in THF at low temperature forms the octahedral complex $Rh(P(CH_3)_3)_2(CO)(C_6H_5)HCl$ (**5**) (Scheme II). When a solution of **5** is warmed to room temperature, the complex eliminates benzene to give $Rh(P(CH_3)_3)_2(CO)Cl$ (**1**). The measured half-life of **5** is approximately 12.3 min at 265 K. In the presence of excess HCl, **1** is in equilibrium with the octahedral complex $Rh(P(CH_3)_3)_2(CO)HCl_2$ (**6**).[12]

Although the reaction of **3** with HCl could give a number of stereoisomers, only one product is observed. The configuration of **5** with the hydride ligand trans to chloride (hydride ligand cis to the phenyl substituent) was established by NOE experiments.[5] In addition, the $^2J_{\mathrm{H\text{-}Rh\text{-}C}}$ coupling between the metal-bound hydride and ^{13}C of the carbonyl was measured to be 4.6 Hz and this small value is characteristic of a cis relationship between the H and CO ligands in such octahedral complexes.[5] At low temperature, the aromatic region of the ^1H NMR spectrum of **5** exhibits five separate resonances and this indicates that rotation of the phenyl group (about the Rh–C bond) is slow on the NMR time scale, making all protons of the monosubstituted phenyl ring nonequivalent. The measured coupling between the metal-bound hydride and ^{13}C of the carbonyl group in **6** is small ($^2J_{\mathrm{H\text{-}Rh\text{-}C}}$ = 3.2 Hz), and this establishes the configuration of **6** to have hydride and carbonyl ligands in a cis relationship.

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(12) (a) Slack, D. A.; Egglestone, D. L.; Baird, M. C. *J. Organomet. Chem.* **1978**, *146*, 71. (b) Behrens, U.; Dahlenburg, L. *J. Organomet. Chem.* **1976**, *116*, 103. (c) Intille, G. M. *Inorg. Chem.* **1972**, *11*, 695.

(13) NMR spectroscopic data for **6**: $^{31}P\{^1H\}$ NMR (THF-d_8, 230 K) δ –3.34 ppm (d, $^1J_{\mathrm{Rh\text{-}P}}$ = 81.1 Hz); ^1H NMR (THF-d_8, 230 K) δ 1.36 (m, $P(CH_3)_3$), –13.29 (dt, Rh-*H*, $^1J_{\mathrm{Rh\text{-}H}}$ = 17.3, $^2J_{\mathrm{P\text{-}H}}$ = 12.7 Hz).

Conclusions

The new complexes $Rh(P(CH_3)_3)_2(CO)CH_3$ (**2**) and $Rh(P(CH_3)_3)_2(CO)Ph$ (**3**) were synthesized from $Rh(P(CH_3)_3)_2(CO)Cl$ (**1**) and all three complexes were examined by X-ray crystallography. The phenyl complex **3** was synthesized by two routes, first by direct substitution of the chloro compound **1** and second from the methyl derivative **2** by irradiation in the presence of benzene. The fact that **2** is photochemically active is significant in that irradation of **2** in the presence of suitable substrates provides a clean route into a range of organorhodium compounds. Since the reaction requires no additional reagents and methane is the only reaction byproduct, isolation of products is not difficult.

$Rh(P(CH_3)_3)_2(CO)Ph$ (**3**) reacts at low temperature with HCl to form the octahedral complex $Rh(P(CH_3)_3)_2(CO)(H)(Cl)Ph$, which is unstable at temperatures above 220 K. The complex thermally eliminates benzene to form $Rh(P(CH_3)_3)_2(CO)Cl$.

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Supplementary Material Available: Tables of thermal parameters and hydrogen atom positional and thermal parameters for 1–3 (6 pages). Ordering information is given on any current masthead page.

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