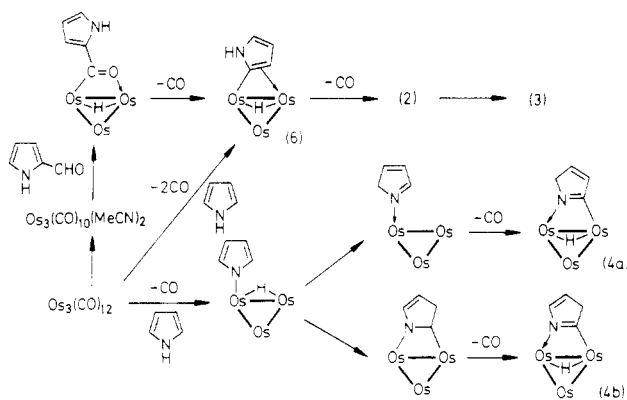**Scheme III**

model, the thermal parameters for the osmium–bonded carbon atom were found to be too small. This situation did not arise in the refinement of molecules A and B of 4. It appears that in this case both molecules are reasonably well ordered, and although it is not possible to make a definitive statement regarding structures 4a and 4b from bond distances and their respective esds, it appears as if molecule B adopts the 4a configuration while molecule A represents a statistical population of both forms, 4a and 4b.

Structure 4b does, however, have some support from analogies we can make with the corresponding chemistry of indole which we find very readily generates (more readily than pyrrole) the analogue of cluster 4 and other clusters containing the same ligand.[22] Only structure 4b would allow the incorporation of a benzo group across a double C=C bond. Structure 4a would require the benzo group of indole to span a single C–C bond of the five-membered ring. This would certainly favor the analogue of 4b for the indole derivative, and probably therefore for the pyrrole compound itself. Such arguments can be

dangerous since pyrrole might indeed adopt structure 4a, but on incorporating the benzo group by using indole, the other isomer might then become the more stable form.

The formation of cluster 4 requires hydrogen atoms to be shifted from the 1- and the 2-positions of pyrrole to the metal atoms to form a hydride and to the 3-position of the ring, respectively. We believe that this process cannot involve the μ,η^2-pyrrolyl cluster $[Os_3H(\mu,\eta^2\text{-}\overline{C=CHCH=CH=NH})(CO)_{10}]$ (6) (Scheme III), since this is almost certainly the intermediate in the decarbonylation of 1 to give 2 initially and then 3 by isomerization. Cluster 6 closely relates to the known furanyl cluster $[Os_3H(\mu,\eta^2\text{-}\overline{C=CHCH=CHO})(CO)_9]$, which has been shown to convert to the furan analogue of 2.[23] Cluster 4 was not detected as a product in the decarbonylation of 1 but was only observed to be formed in the direct reaction of $[Os_3(CO)_{12}]$ with pyrrole. Scheme III contains a proposed route for its formation. We believe that 4 is formed as a results of oxidative addition of pyrrole with N–H cleavage in contrast to the C–H cleavage which leads to 2 and 3. Various hydrogen-transfer reactions could lead to either 4a or 4b. Clearly many of the details of this are speculative, and it is possible but we feel unlikely that the unstable tautomers A or B (Figure 1) are in sufficient concentration in equilibrium with pyrrole to react directly and competitively with pyrrole itself.

Supplementary Material Available: Tables of anisotropic displacement factors and least-squares planes for 1, 3, and 4 (8 pages); listings of observed and calculated structure factors (94 pages). Ordering information is given on any current masthead page.

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Carbon–Oxygen Bond Formation on Rhodium Centers. Synthesis, Characterization, Crystal Structure, and Reactions of *trans*-PhORh(CO)(PPh3)2

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The synthesis of a rhodium phenoxide is reported. The complex *trans*-PhORh(CO)(PPh$_3$)$_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 15.794 (3) Å, b = 11.449 (2) Å, c = 20.025 (3) Å, β = 100.220 (13)°, V = 3562 (1) Å^3, and Z = 4. Diffraction data (Mo Kα, 2θ = 4.5–50.0°) were collected with a Syntex P2$_1$ diffractometer, and the structure was refined to R_F = 2.8% for 5293 reflections. The structure is isomorphous with the iridium analogue. Important dimensions include Rh–P = 2.337 (1)–2.357 (1) Å, Rh–CO = 1.801 (3) Å, Rh–OPh = 2.044 (2) Å, and Rh–O–C(phenoxide) = 125.52 (19)°. This complex reacts with Ph$_2$CHC(O)Cl to give the ester Ph$_2$CHC(O)OPh and with MeI to give anisole, PhOMe. The formation of anisole from the rhodium phenoxide is in contrast to the failure to eliminate ethers from similar iridium complexes and is consistent with the known preference for elimination from second-row (rather than third-row) transition-metal complexes.

Carbon–oxygen bond formation is important in several catalytic reactions.[2–5] A few reports of the stoichiometric

formation of esters from reactions of acyl sources with alkoxy complexes have appeared.[6–9] In this paper we show

that *trans*-PhORh(CO)(PPh$_3$)$_2$ reacts with MeI to give anisole and *trans*-Rh(CO)(PPh$_3$)$_2$I and also reacts with Ph$_2$CHC(O)Cl to yield Ph$_2$CHC(O)OPh and *trans*-Rh-(CO)(PPh$_3$)$_2$Cl.

The study of metal alkoxide and aryloxide complexes has become an active area of investigation for a number of groups.[10] We have examined the reactions of iridium alkoxides with acyl and alkyl sources in order to study C–O bond-forming reactions.[7–9] Reactions with acid chlorides give esters, but reactions with MeI do not give ethers.[7,8a] To further examine possible C–O bond formation, we have now prepared a phenoxy–rhodium complex.[11]

Experimental Section

trans-Rh(CO)(PPh$_3$)$_2$Cl was purchased from Strem Chemical Co. Methyl iodide was purchased from Mallinckrodt. All solvents were dried and degassed prior to use. All syntheses were accomplished under a nitrogen, argon, or vacuum atmosphere. Infrared spectra were recorded on a Beckman 4240 spectrometer, and ^{1}H NMR spectra were recorded on a Varian EM 390 or on a JEOL FX90Q instrument. Elemental analysis was performed by Oneida Research Services. Gas chromatography was performed on a Varian 2440-FID gas chromatograph.

trans-PhORh(CO)(PPh$_3$)$_2$. A mixture of 0.4 g of *trans*-Rh(CO)(PPh$_3$)$_2$Cl and 0.5 g of NaOPh in 50 mL of THF was stirred in an inert-atmosphere glovebox for 18 h. The THF was removed and the solid extracted with 75 mL of C$_6$H$_6$/C$_6$H$_{12}$. The solvent was removed to yield a yellow powder. Recrystallization from C$_6$H$_{12}$ gave yellow crystals. IR (C$_6$H$_{12}$): 1975 cm^{-1}. Anal. Calcd: C, 68.98; H, 4.68. Found: C, 68.98; H, 4.68.

Reaction with MeI. A solution of *trans*-PhORh(CO)(PPh$_3$)$_2$ (0.03 g) in 25 mL of benzene was removed from the inert-atmosphere glovebox. Purified MeI (0.4 mL) was added under N$_2$ and the reaction mixture stirred overnight. The yellow solution slowly turned to burnt orange. A ^{1}H NMR spectrum of the reaction mixture showed a singlet at 3.28 ppm, which was identified as anisole by comparison with an authentic sample. Gas chromatographic analysis on an Anakrom column at 110 °C confirmed the presence of anisole in 68% yield. The solvent was removed and the burnt orange solid dissolved in C$_6$H$_{12}$. An infrared spectrum gave a ν_{CO} band at 1982 cm^{-1}. The properties of this complex were identical with those of independently prepared *trans*-Rh(CO)(PPh$_3$)$_2$I.

Reaction with Ph$_2$CHC(O)Cl. A solution of 0.025 g of *trans*-PhORh(CO)(PPh$_3$)$_2$ and 0.016 g of Ph$_2$CHC(O)Cl in 5 mL of C$_6$H$_{12}$ was stirred overnight in an inert-atmosphere glovebox. A yellow precipitate formed, which was filtered off and shown to be *trans*-Rh(CO)(PPh$_3$)$_2$Cl (ν_{CO} = 1965 (br) in C$_6$H$_6$). An infrared spectrum of the solution showed absorbances at 1800 and 1760 cm^{-1}. The 1800-cm^{-1} absorbance is due to Ph$_2$CHC(O)Cl. The 1760-cm^{-1} absorbance was due to Ph$_2$CHC(O)OPh, which formed quantitatively and was identified by comparison of the infrared absorbance to that of a known sample.

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Table I. Experimental Data for the X-ray Diffraction Study of *trans*-PhORh(CO)(PPh$_3$)$_2$

(A) Unit Cell Parameters	
cryst syst: monoclinic	V = 3562 (1) Å^3
space group: $P2_1/c$ (No. 14)	Z = 4
a = 15.794 (3) Å	formula: C$_{43}$H$_{35}$O$_2$P$_2$Rh
b = 11.449 (2) Å	mol wt: 748.6
c = 20.025 (3) Å	D(calcd) = 1.396 g cm^{-3}
β = 100.220 (13)°	T = 24 °C (297 K)

(B) Collection of X-ray Diffraction Data

diffractometer: Synthex P2$_1$
radiation: Mo Kα ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: highly oriented (pyrolytic) graphite; equatorial mode with 2θ(m) = 12.160°; assumed to be 50% perfect, 50% ideally mosaic for polarizn cor
rflns measd: +h,+k,±l for 2θ = 4.5–50.0°; 6108 reflns collected and merged to 5293 unique data
scan conditions: coupled θ(cryst)–2θ(counter), at 4.0° min^{-1} in 2θ, from [2θ(Kα_1) – 0.9]° through [2θ(Kα_2) + 0.9]°.
bkgds: stationary cryst, stationary counter at the two extremes of the 2θ scan; each for one-fourth of the total scan time
std reflns: three mutually orthogonal rflns collected before each set of 97 data points; no decay or any signif fluctuations obsd

Collection of X-ray Diffraction Data for *trans*-PhORh-(CO)(PPh$_3$)$_2$. The crystal used for data collection has a yellow parallelepiped of approximate dimensions 0.3 × 0.2 × 0.2 mm. It was sealed into a thin-walled capillary and aligned (with its extended axis close to coincident with the instrumental ϕ axis) on a Syntex P2$_1$ four-circle diffractometer. Setup operations and data collection were carried out as described previously (see Table I).[14] The observed diffraction symmetry ($2/m$) and the systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$) are consistent only with the ubiquitous centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14).
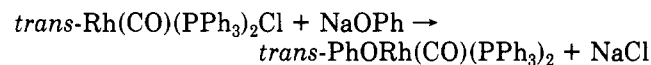
All data were corrected for Lorentz and polarization effects, were converted to $|F_o|$ values, and were placed upon an absolute scale by means of a Wilson plot. A survey of several ψ scans of close-to-axial reflections (I_{min}/I_{max} = 0.97) indicated that absorption could safely be ignored.

Solution and Refinement of the Crystal Structure. The structure was solved by means of a Patterson map, which revealed the position of the single independent rhodium atom. All other non-hydrogen atoms were located from a difference-Fourier map. Hydrogen atoms were placed in idealized positions with d(C–H) = 0.95 Å.[15] Full-matrix least-squares refinement converged (($\Delta/\sigma)_{max}$ = 0.05) with R_F = 2.8%, R_{wF} = 3.7%, and GOF = 1.10 for all 5293 reflections. A final difference-Fourier synthesis showed no significant residuals. Final positional parameters are collected in Table II.

The structural study was carried out with analytical scattering factors for neutral atoms with corrections for anomalous dispersion.[16]

Results and Discussion

Reaction of NaOPh with *trans*-Rh(CO)(PPh$_3$)$_2$Cl resulted in the production of the rhodium phenoxide, *trans*-PhORh(CO)(PPh$_3$)$_2$:[11]

trans-Rh(CO)(PPh$_3$)$_2$Cl + NaOPh →
$\qquad\qquad\qquad$ *trans*-PhORh(CO)(PPh$_3$)$_2$ + NaCl

The characterizations are all consistent with the formulation. Attempts to use alkoxides in similar syntheses result in at least two facile decomposition modes.[17] Rhodium alkoxides are less stable than the analogous

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Table II. Final Positional Parameters for *trans*-PhORh(CO)(PPh₃)₂

atom	x	y	z	atom	x	y	z
C(1)	0.2670 (2)	0.1597 (3)	-0.2727 (1)	C(66)	0.4196 (2)	-0.1756 (3)	-0.0898 (2)
C(2)	0.2297 (2)	-0.2415 (3)	-0.2240 (1)	O(1)	0.2857 (2)	0.2473 (2)	-0.2942 (1)
C(3)	0.1921 (3)	-0.3426 (3)	-0.2027 (2)	O(2)	0.2027 (1)	-0.1374 (2)	-0.2075 (1)
C(4)	0.2172 (4)	-0.4518 (3)	-0.2209 (2)	P(1)	0.1416 (0)	0.0049 (1)	-0.3472 (0)
C(5)	0.2805 (3)	-0.4646 (3)	-0.2599 (2)	P(2)	0.3386 (0)	0.0337 (1)	-0.1428 (0)
C(6)	0.3169 (3)	-0.3672 (3)	-0.2815 (2)	Rh(1)	0.2380 (0)	0.0192 (0)	-0.2432 (0)
C(7)	0.2920 (2)	-0.2566 (3)	-0.2648 (2)	H(3A)	0.1488	-0.3361	-0.1756
C(11)	0.1947 (2)	-0.0238 (3)	-0.4199 (1)	H(4A)	0.1907	-0.5195	-0.2064
C(12)	0.2603 (2)	0.0496 (4)	-0.4315 (2)	H(5A)	0.2985	-0.5402	-0.2713
C(13)	0.3017 (2)	0.0330 (4)	-0.4861 (2)	H(6A)	0.3600	-0.3753	-0.3088
C(14)	0.2798 (3)	-0.0600 (4)	-0.5292 (2)	H(7A)	0.3179	-0.1899	-0.2811
C(15)	0.2148 (4)	-0.1313 (4)	-0.5189 (2)	H(12A)	0.2770	0.1130	-0.4014
C(16)	0.1717 (3)	-0.1141 (3)	-0.4649 (2)	H(13A)	0.3453	0.0857	-0.4937
C(21)	0.0533 (2)	-0.1015 (3)	-0.3576 (1)	H(14A)	0.3098	-0.0740	-0.5656
C(22)	0.0721 (2)	-0.2190 (3)	-0.3467 (2)	H(15A)	0.1989	-0.1947	-0.5491
C(23)	0.0063 (3)	-0.3011 (3)	-0.3548 (2)	H(16A)	0.1261	-0.1641	-0.4593
C(24)	-0.0781 (3)	-0.2681 (4)	-0.3736 (2)	H(22A)	0.1301	-0.2434	-0.3334
C(25)	-0.0972 (2)	-0.1522 (4)	-0.3848 (2)	H(23A)	0.0197	-0.3813	-0.3472
C(26)	-0.0325 (2)	-0.0679 (3)	-0.3767 (2)	H(24A)	-0.1230	-0.3244	-0.3789
C(31)	0.0867 (2)	0.1448 (3)	-0.3680 (1)	H(25A)	-0.1555	-0.1286	-0.3982
C(32)	0.0604 (2)	0.2058 (3)	-0.3158 (2)	H(26A)	-0.0468	0.0123	-0.3842
C(33)	0.0182 (3)	0.3117 (4)	-0.3279 (2)	H(32A)	0.0712	0.1745	⁻0.2712
C(34)	0.0038 (3)	0.3578 (3)	-0.3919 (2)	H(33A)	-0.0005	0.3527	-0.2919
C(35)	0.0305 (3)	0.2989 (3)	-0.4438 (2)	H(34A)	-0.0246	0.4307	-0.4002
C(36)	0.0710 (2)	0.1914 (3)	-0.4326 (2)	H(35A)	0.0212	0.3321	-0.4881
C(41)	0.4090 (2)	0.1625 (3)	-0.1296 (1)	H(36A)	0.0879	0.1501	-0.4691
C(42)	0.3722 (2)	0.2731 (3)	-0.1389 (2)	H(42A)	0.3116	0.2806	-0.1528
C(43)	0.4228 (3)	0.3728 (3)	-0.1283 (2)	H(43A)	0.3969	0.4481	-0.1350
C(44)	0.5104 (3)	0.3624 (4)	-0.1082 (2)	H(44A)	0.5453	0.4305	-0.1011
C(45)	0.5480 (2)	0.2537 (4)	-0.0984 (2)	H(45A)	0.6085	0.2470	-0.0840
C(46)	0.4979 (2)	0.1535 (3)	-0.1091 (2)	H(46A)	0.5242	0.0787	-0.1026
C(51)	0.2965 (2)	0.0282 (3)	-0.0635 (1)	H(52A)	0.1949	-0.0768	-0.0988
C(52)	0.2233 (2)	-0.0361 (3)	-0.0599 (2)	H(53A)	0.1417	-0.0880	0.0018
C(53)	0.1912 (3)	-0.0419 (4)	-0.0002 (2)	H(54A)	0.2072	0.0159	0.0969
C(54)	0.2303 (3)	0.0181 (4)	0.0562 (2)	H(55A)	0.3312	0.1225	0.0927
C(55)	0.3035 (3)	0.0815 (4)	0.0535 (2)	H(56A)	0.3870	0.1313	-0.0068
C(56)	0.3366 (2)	0.0869 (3)	-0.0056 (2)	H(62A)	0.4560	-0.0417	-0.2255
C(61)	0.4129 (2)	-0.0892 (3)	-0.1390 (1)	H(63A)	0.5453	-0.2033	-0.2294
C(62)	0.4601 (2)	-0.1002 (3)	-0.1914 (2)	H(64A)	0.5540	-0.3480	-0.1465
C(63)	0.5128 (2)	-0.1965 (3)	-0.1940 (2)	H(65A)	0.4764	-0.3309	-0.0603
C(64)	0.5183 (2)	-0.2819 (3)	-0.1450 (2)	H(66A)	0.3875	-0.1693	-0.0528
C(65)	0.4724 (2)	-0.2715 (3)	-0.0937 (2)				

iridium alkoxides.[18] To ascertain a possible structural reason for the lowered stability, we have determined the structure of *trans*-PhORh(CO)(PPh₃)₂.

Description of the Structure of *trans*-PhORh-(CO)(PPh₃)₂. The complex crystallizes as discrete molecular units, with no unusually short contacts between the molecules. The atomic labeling is illustrated in Figure 1. Interatomic distances and angles of interest are compiled in Table III. The structure is isomorphous with that of the previously reported[19] iridium analogue *trans*-PhOIr-(CO)(PPh₃)₂.

The central d⁸ rhodium(I) atom has a square-planar coordination environment with trans angles P(1)–Rh–P(2) = 177.45 (3)° and C(1)–Rh–O(2) = 178.01 (12)° (cf. P-(1)–Ir–P(2) = 178.15 (4)° and C(1)–Ir–O(2) = 178.19 (20)° in the iridium analogue).[19]

The two independent rhodium–phosphorus distances are inequivalent with Rh–P(1) = 2.357 (1) Å and Rh–P(2) = 2.337 (1) Å (cf. 2.344 (1) and 2.328 (1) Å for the Ir complex). We assume that this statistically significant (but chemically unimportant) spread arises from asymmetry in the crystallographic packing.

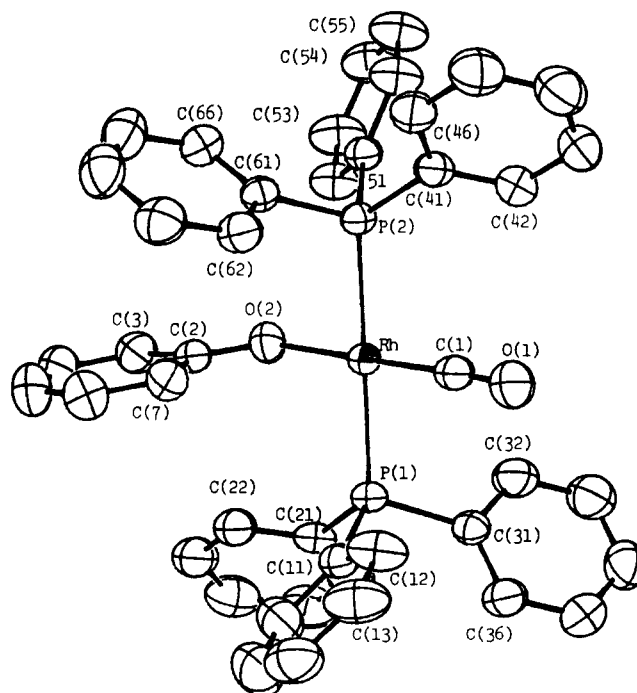Distances and angles within the PPh₃ ligands are normal, with P–C = 1.825 (3)–1.838 (3) Å, C–C = 1.356

Figure 1. ORTEP diagram showing the labeling of non-hydrogen atoms in the *trans*-PhORh(CO)(PPh₃)₂ molecule. Atoms within each phenyl group are numbered consecutively in a cyclic fashion, with the ipso carbon having the lowest number.

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Table III. Important Interatomic Distances (Å) and Angles (deg) for *trans*-PhORh(CO)(PPh₃)₂

(A) Rhodium–Ligand Distances

Rh–P(1)	2.357 (1)	Rh–O(2)	2.044 (2)
Rh–P(2)	2.337 (1)	Rh–C(1)	1.801 (3)
C(1)–O(1)	1.151 (4)	Rh···O(1)	2.950 (2)

(B) Phosphorus–Carbon Distances

P(1)–C(11)	1.834 (3)	P(2)–C(41)	1.838 (3)
P(1)–C(21)	1.836 (3)	P(2)–C(51)	1.828 (3)
P(1)–C(31)	1.834 (3)	P(2)–C(61)	1.825 (3)

(C) Distances within the Phenoxide Ligand

C(2)–C(3)	1.402 (4)	C(5)–C(6)	1.360 (6)
C(3)–C(4)	1.380 (5)	C(6)–C(7)	1.384 (5)
C(4)–C(5)	1.381 (7)	C(7)–C(2)	1.397 (5)
C(2)–O(2)	1.327 (4)		

(D) Range of C–C Distances in PPh₃ Ligands
1.356 (6)–1.397 (4) (av 1.382 Å)

(E) Angles about Rhodium

P(1)–Rh–P(2)	177.45 (3)	P(2)–Rh–C(1)	92.59 (9)
P(1)–Rh–C(1)	86.23 (9)	P(2)–Rh–O(2)	86.98 (6)
P(1)–Rh–O(2)	94.28 (6)	C(1)–Rh–O(2)	178.01 (12)
Rh–C(1)–O(1)	177.06 (28)		

(F) Rh–P–C and C–P–C Angles

Rh–P(1)–C(11)	113.52 (10)	C(11)–P(1)–C(21)	103.66 (14)
Rh–P(1)–C(21)	120.33 (10)	C(11)–P(1)–C(31)	103.92 (14)
Rh–P(1)–C(31)	110.20 (9)	C(21)–P(1)–C(31)	103.58 (14)
Rh–P(2)–C(41)	118.85 (10)	C(41)–P(2)–C(51)	101.93 (14)
Rh–P(2)–C(51)	116.64 (10)	C(41)–P(2)–C(61)	104.16 (14)
Rh–P(2)–C(61)	108.37 (9)	C(51)–P(2)–C(61)	105.51 (13)

(G) Angles Involving C(2) and O(2) of the Phenoxide Ligand

Rh–O(2)–C(2)	125.52 (19)	O(2)–C(2)–C(7)	123.20 (27)
O(2)–C(2)–C(3)	119.58 (30)		

(H) C(ortho)–C(ipso)–C(ortho) Angles of Phenyl Groups

C(12)–C(11)–C(16)	117.64 (31)	C(42)–C(41)–C(46)	118.76 (29)
C(22)–C(21)–C(26)	118.76 (31)	C(52)–C(51)–C(56)	118.34 (29)
C(32)–C(31)–C(36)	119.06 (30)	C(62)–C(61)–C(66)	119.07 (28)
C(3)–C(2)–C(7)	117.15 (29)		

(I) P–C–C Angles

P(1)–C(11)–C(12)	119.03 (24)	P(2)–C(41)–C(42)	118.89 (24)
P(1)–C(11)–C(16)	123.31 (27)	P(2)–C(41)–C(46)	122.33 (25)
P(1)–C(21)–C(22)	119.27 (26)	P(2)–C(51)–C(52)	119.98 (23)
P(1)–C(21)–C(26)	121.97 (26)	P(2)–C(51)–C(56)	121.68 (24)
P(1)–C(31)–C(32)	117.61 (24)	P(2)–C(61)–C(62)	117.59 (23)
P(1)–C(31)–C(36)	123.33 (24)	P(2)–C(61)–C(66)	123.16 (24)

(6)–1.397 (4) Å, Rh–P–C(ipso) = 108.37 (9)–120.33 (10)°, C–P–C = 101.93 (14)–105.51 (13)°, and C–C(ipso)–C = 117.64 (31)–119.07 (28)°.

The Rh–C–O system is essentially linear, with Rh–C(1) = 1.801 (3) Å, C(1)–O(1) = 1.151 (4) Å, and Rh–C(1)–O(1) = 177.06 (28)° (cf. Ir–C = 1.795 (5) Å, C–O = 1.162 (7) Å, and Ir–C–O = 176.8 (5)° for the Ir species).

The phenoxide ligand is linked to rhodium via the bond Rh–O(2) = 2.044 (2) Å, with Rh–O(2)–C(2) = 125.52 (19)° (cf. 2.049 (4) Å and 126.5 (3)° for the Ir complex). The O(2)–C(2) bond length is 1.327 (4) Å (cf. 1.324 (6) Å in the Ir complex). The internal angle at the ipso carbon of the phenoxide ligand is reduced to 117.15 (29)°, due to the electronegative nature of the attached oxygen atom.[20] The structure of (PMe₃)₃Rh(Otol)(HOtol) was briefly reported.[21] The presence of the hydrogen bond has only a slight effect on the Rh–O–C angle (121.5 versus 125.5° for *trans*-PhORh(CO)(PPh₃)₂). The Rh–O bond length was not reported for (PMe₃)₃Rh(Otol)(HOtol), precluding a more detailed comparison.[21]

Finally, we note that the covalent radii of rhodium(I) and iridium(I) are essentially equivalent in *trans*-PhOM-(CO)(PPh₃)₂ (M = Rh, Ir). The differences in bond length, Δ, defined by d(Rh–X) – d(Ir–X), are +0.011 Å for M–P, +0.006 Å for M–CO, and –0.005 Å for M–OPh. Similar results have been noted for M–P, M–CO, and M–Cl distances in *trans*-M(CO)(PPh₃)₂Cl (M = Rh, Ir; see Table 6 of ref 22).

Reductive-Elimination Reactions. Reaction of *trans*-PhORh(CO)(PPh₃)₂ with methyl iodide in cyclohexane gave anisole (68%) and *trans*-Rh(CO)(PPh₃)₂I:

trans-PhORh(CO)(PPh₃)₂ + MeI →
   trans-Rh(CO)(PPh₃)₂I + PhOMe   (1)

Anisole was identified by ¹H NMR and gas chromatographic comparison to an authentic sample. Reaction of *trans*-PhORh(CO)(PPh₃)₂ with Ph₂CHC(O)Cl gives the ester Ph₂CHC(O)OPh and *trans*-Rh(CO)(PPh₃)₂Cl:

trans-PhORh(CO)(PPh₃)₂ + Ph₂CHC(O)Cl →
   trans-Rh(CO)(PPh₃)₂Cl + Ph₂CHC(O)OPh   (2)
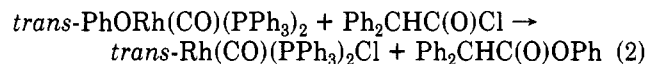
This reaction occurs quantitatively.

The formation of an ester by reaction of *trans*-PhORh(CO)(PPh₃)₂ with an acid chloride is consistent with observations on analogous iridium complexes, *trans*-ROIr(CO)L₂.[7,8] A report of similar reactions appeared previously.[6] The formation of anisole by the reaction of MeI with *trans*-PhORh(CO)(PPh₃)₂ is more unusual. In two cases, treatment of an alkoxy transition-metal complex with MeI (neat) has resulted in ether elimination.[23,24] Thus, a 16% yield of anisole was observed on treatment of Fe(OPh)₂(bpy) with MeI;[23] an unspecified yield of dimethyl ether was observed from the reaction of Pt(dppe)(Me)(OMe) with MeI.[24] Oxidative addition of MeI to iridium(I) analogues leads to reasonably stable Ir(III) complexes that do not eliminate ethers even upon decomposition.[7,8] The relatively greater stability of Ir(III) over that of Rh(III) is well documented. Perhaps the preference for Rh(I) over Rh(III) leads to the elimination of anisole in reaction 1.[25] The rhodium products (*trans*-Rh(CO)(PPh₃)₂X, X = Cl, I) from reactions 1 and 2 also show the preference for Rh(I).

The preference for reductive-elimination reactions involving palladium vis-à-vis platinum is well documented.[29] Calculations suggest a 30 kcal/mol difference in the activation barrier.[29] The same preference for the second-row metal is apparent for rhodium versus iridium, though perhaps not to that magnitude.

While iridium(I) complexes *trans*-Ir(CO)(PPh₃)₂X readily add RX to give Ir(III) complexes, the rhodium analogues require high concentrations (often neat MeI) to drive similar reactions.[30,31] In our reactions in benzene

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solution, the concentration of MeI is insufficient to drive the equilibrium to Rh(Me)(I)$_2$(CO)(PPh$_3$)$_2$ and *trans*-Rh-(CO)(PPh$_3$)$_2$I is observed as the rhodium product. The failure of Ph$_2$CHC(O)Cl to add to *trans*-Rh(CO)(PPh$_3$)$_2$Cl may also indicate the greater stability of Rh(I) over that of Rh(III), although in this case the lack of solubility of *trans*-Rh(CO)(PPh$_3$)$_2$Cl may also be a significant factor.

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Synthesis of Extremely Stable Alkyl and Hydride Complexes of the Type (R₂NCS₂)Pt(PEt₃)R

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The reaction of (R$_2$NCS$_2$)Pt(PEt$_3$)Cl (R = Me, Et), prepared from [Pt(PEt$_3$)Cl$_2$]$_2$ and Na(R$_2$NCS$_2$), with alkyllithium or Grignard reagents yields (R$_2$NCS$_2$)Pt(PEt$_3$)(alkyl) (alkyl = Me, *n*-Pr, *i*-Pr, *n*-Bu, *sec*-Bu, *i*-Bu, *t*-Bu) complexes. These new alkylplatinum complexes are very stable and can be heated in solution at 100 °C for extended periods without decomposition. The reaction of (R$_2$NCS$_2$)Pt(PEt$_3$)Cl with NaBH$_4$ yields the stable complexes (R$_2$NCS$_2$)Pt(PEt$_3$)H, which decompose only slowly at 110 °C. This hydride (R = Me) does not react with ethylene or phenylacetylene but will react with MeO$_2$CC≡CCO$_2$Me to yield a mixture of the *E* and *Z* isomers of (Me$_2$NCS$_2$)Pt(PEt$_3$)(η^1-C(CO$_2$Me)=C(H)CO$_2$Me). The reaction of (R$_2$NCS$_2$)Pt(PEt$_3$)Cl with AgBF$_4$ and ethylene yields [(R$_2$NCS$_2$)Pt(PEt$_3$)(C$_2$H$_4$)]BF$_4$, but these complexes are very unstable, decomposing rapidly in the absence of ethylene. The complexes (Me$_2$NCS$_2$)PtLCl (L = CO, C$_2$H$_4$) are prepared by mixing the L ligand with [Pt(Me$_2$NCS$_2$)Cl]$_2$.

Introduction

The investigation of the synthesis and reactivity of alkylmetal complexes is central to the understanding of many processes catalyzed by transition metals.[1] An important example of a catalytic process involving alkylmetal intermediates is the hydroformylation reaction.[2] Continuing our interest in alkylmetal complexes, we desired flexible and direct synthetic routes to neutral complexes of platinum that contain one alkyl ligand of the general formula (A-A)PtL(alkyl), where A-A is a bidentate, monoanionic ligand and L is a neutral, two-electron-donor ligand. A number of (A-A)PtLX (X = halide) type starting materials are known, as are a few (A-A)PtL(alkyl) complexes.[3] We anticipated that this class of compounds, containing classic coordination chemistry ligands, would yield stable new alkylmetal complexes useful for a number of desired model studies relating to the hydroformylation reaction.

Described here are efforts directed at the synthesis of these (A-A)PtL(alkyl) complexes, where (A-A)⁻ is the dialkyldithiocarbamato ligand and L is PEt$_3$. We report that dialkyldithiocarbamato complexes, (R$_2$NCS$_2$)Pt(PEt$_3$)-(alkyl) (R = Me, Et), are readily synthesized for a wide variety of alkyl groups and are extremely stable. The extremely stable hydride complexes (R$_2$NCS$_2$)Pt(PEt$_3$)H are readily prepared and react (R = Me) with MeO$_2$CC≡CCO$_2$Me to yield a mixture of the *E* and *Z* isomers of (Me$_2$NCS$_2$)Pt(PEt$_3$)[η^1-C(CO$_2$Me)=C(H)CO$_2$Me]. We also report the synthesis of [(R$_2$NCS$_2$)Pt(PEt$_3$)(C$_2$H$_4$)]BF$_4$ and (R$_2$NCS$_2$)PtLCl (L = CO, C$_2$H$_4$) complexes.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere with use of either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. The ¹H and ³¹P NMR spectra were recorded on a Bruker AM300 spectrometer using a 5-mm broad-band probe. An IBM NR-80 spectrometer was used to obtain ¹³C NMR spectra. ¹H and ³¹P NMR chemical shifts are reported in ppm versus TMS and H$_3$PO$_4$, respectively. The triethylphosphine proton resonances are seen

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