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Reactions of Carbon Monoxide with Phosphine Adducts of $Nb(2,4\text{-}C_7H_{11})_2$: Spontaneous Reduction to Niobium(I) Complexes

Thomas E. Waldman,[1] Beth Waltermire,[2] Arnold L. Rheingold,*[,2] and Richard D. Ernst*[,1]

Departments of Chemistry, University of Utah, Salt Lake City, Utah 84112, and University of Delaware, Newark, Delaware 19716

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The reactions of 17 electron $Nb(2,4\text{-}C_7H_{11})_2(L)$ species ($L = PEt_3$, $PMe_2C_6H_5$) with CO lead to the loss of one pentadienyl ligand and formation of the 18 electron Nb(I) complexes $Nb(2,4\text{-}C_7H_{11})(L)(CO)_3$ in high yield. One carbonyl ligand may be thermally replaced by a second equivalent of phosphine, yielding "*trans*"-$Nb(2,4\text{-}C_7H_{11})(PMe_2Ph)_2(CO)_2$, which adopts something close to a piano-stool geometry with the phosphines located by the open dienyl edge and the central dienyl carbon atom. The $Nb(2,4\text{-}C_7H_{11})(L)(CO)_3$ complexes are also susceptible to reduction by alkali metals, presumably leading to $Nb(2,4\text{-}C_7H_{11})(CO)_3^{2-}$. Oxidation of these species under CO leads to $Nb(2,4\text{-}C_7H_{11})(CO)_4$. Structural determinations have been carried out for $Nb(2,4\text{-}C_7H_{11})(PMe_2Ph)(CO)_3$ and $Nb(2,4\text{-}C_7H_{11})(PMe_2Ph)_2(CO)_2$. For the former the space group is $P\bar{1}$ with $a = 7.911(5)$ Å, $b = 10.490(6)$ Å, $c = 12.829(6)$ Å, $\alpha = 105.61(4)°$, $\beta = 95.88(4)°$, $\gamma = 107.59(4)°$, and $V = 957.5(8)$ Å^3 for $Z = 2$. The structure has been refined to discrepancy indices of $R = 0.031$ and $R_w = 0.034$. For the latter the space group is $P2_1/c$ with $a = 11.778(2)$ Å, $b = 13.966(2)$ Å, $c = 15.930(3)$ Å, $\beta = 96.33(1)°$ for $Z = 4$. The structure was refined to discrepancy indices of $R = 0.037$ and $R_w = 0.039$.

Titanocene and vanadocene are known as 18-electron dicarbonyl[3] and 17-electron monocarbonyl[4] complexes. In contrast, various electron deficient open titanocene and open vanadocene complexes react readily with CO only to yield monocarbonyl complexes, possessing 16- and 17-electron counts, respectively.[5] The inability of the open titanocene to incorporate a second carbonyl ligand may be traced to the much greater steric demand of pentadienyl ligands relative to C_5H_5 and even C_5Me_5. One might then expect that the steric demands of the dienyl ligands could be offset by the larger metals in the second or third transition series, and indeed, the 18-electron complex $Zr(2,4\text{-}C_7H_{11})_2(CO)_2$ may be isolated from $Zr(2,4\text{-}C_7H_{11})_2(PEt_3)$, although it readily reverts to a monocarbonyl as well.[6] It was therefore of interest to investigate related reactions for phosphine adducts of $Nb(2,4\text{-}C_7H_{11})_2$.[7] In fact, again some unique behavior is observed, as one pentadienyl ligand is spontaneously lost under CO, leading to the 18-electron Nb(I) complexes $Nb(dienyl)(CO)_3(L)$ ($L = PEt_3$, PMe_2Ph). These and related results are described herein.

Experimental Section

The compounds described exhibit varying degrees of air sensitivity and were therefore prepared, handled, and stored under nitrogen atmospheres. Hydrocarbon and ethereal solvents were predried and distilled under nitrogen from Na/benzophenone prior to use. Magnetic and spectroscopic data were obtained as previously described.[8] The starting diene,[9] dienyl anion,[10] $NbCl_4(THF)_2$,[11] and phosphines[12] were either prepared by reported procedures or purchased.

$Nb(2,4\text{-}C_7H_{11})_2(PMe_2Ph)$. A 250-mL three-neck flask equipped with a magnetic stirring bar, nitrogen inlet, and dropping funnel was charged with 2.00 g (5.28 mmol) of $NbCl_4(THF)_2$ and 100 mL of THF. Dimethylphenylphosphine (0.75 mL, 5.3 mmol) was added via syringe to the stirred yellow suspension, resulting in immediate reaction to yield a dark green solution. After the solution was cooled to −78 °C, 2.91 g (21.6 mmol) of potassium 2,4-dimethylpentadienide in 50 mL of THF was added dropwise to the green solution. Addition was complete in ca. 10 min, during which time the solution had assumed a deep maroon color. The reaction mixture was then warmed to ambient temperature and stirred at this temperature for 1 h. At the end of this time the solution was dark green-brown and the solvent was removed in vacuo, resulting in a green-brown solid. Extraction of the solids with five 50-mL portions of diethyl ether and filtration through a Celite pad on a coarse frit gave a dark green filtrate. The dark green filtrate was concentrated in vacuo to ca. 100 mL and then cooled at −20 °C for 12 h, during which time deep green crystals of the product formed. The supernatant was transferred to a clean flask, and the crystals (1.07 g, mp 138–140 °C dec) were dried in vacuo. Further concentration of the supernatant and cooling at −20 °C for 2 days resulted in an additional 0.44 g of product, for an overall yield of 68%. IR (Nujol mull): 2970 (vs, br), 1455 (s), 1430 (shoulder), 1372 (s, sh), 1365 (shoulder), 1325 (vw), 1275 (w, sh), 1158 (w), 1021 (m, sh), 998 (m), 928 (m, vsh), 911 (m, sh), 900 (s, sh), 861 (w), 848 (w), 833 (m), 819 (m, sh), 788 (m), 745 (ms, sh), 739 (ms, sh), 720 (m), 697 (ms, sh) cm^{-1}. Mass spectrum (EI, 17 eV; *m/z* (relative

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[2] University of Delaware.

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intensity)): 421 (0.6), 283 (14), 138 (100), 123 (64), 121 (21), 91 (13). Anal. Calcd for $C_{22}H_{33}NbP$: C, 62.71; H, 7.89. Found: C, 62.47; H, 8.10. ESR (toluene): a = 120.6 G.

$Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)$. A 250-mL two-neck flask equipped with a magnetic stirring bar and gas inlet was charged with 0.44 g (1.0 mmol) of $Nb(2,4\text{-}C_7H_{11})_2(PMe_2Ph)$ and 50 mL of THF. The resulting deep green solution was saturated with carbon monoxide and then stirred vigorously under an atmosphere of carbon monoxide. After being stirred for ca. 72 h the solution had become a deep blood red and the solvent was removed in vacuo; the resulting red oil was extracted with four 50-mL portions of hexane and filtered through a Celite and silica pad. The bright red hexane filtrate was concentrated in vacuo to ca. 15 mL and cooled to −20 °C, and after several hours blood red, needlelike crystals began to form. After it was cooled for an additional 12 h, the supernatant was removed by syringe and the product dried in vacuo, yielding 0.32 g (0.77 mmol, 74% yield) of moderately air-sensitive red needles of $Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)$, mp 118–120 °C dec. ^1H NMR (benzene-d_6, ambient): δ 7.23–7.01 (m, 5H, Ph), 5.17 (s, 1H, H-3), 2.90 (s, 2H, $H_{1,5\,exo}$), 1.80 (s, 6H, CH_3-Pdl), 1.44 (d, 6H, J = 5.9 Hz, PCH_3), 0.56 (d, 2H, J = 7.3 Hz, $H^{1,5}_{endo}$). ^{13}C NMR (benzene-d_6, ambient): δ 260.5 (s, 2C, CO), 249.2 (s, 1C, CO), 129.8–127.5 (m, 6C, P*Ph*), 122.4 (s, 2C, C-2,4), 88.7 (d, 1C, J = 158.9 Hz, C-3), 68.1 (t, 2C, J = 154.8 Hz, C-1,5), 29.4 (q, 2C, J = 126.5 Hz, CH_3-Pdl), 17.3 (q of d, 2C, J = 129.8, 23 Hz, P(CH_3)). ^{31}P NMR (benzene-d_6, ambient): δ 28.65. IR (Nujol mull): 2930 (vs, br), 1961 (vs, sh), 1870 (vs, br), 1522 (vw), 1460 (s, br), 1370 (m, sh), 1155 (w, sh), 1098 (vw, br), 1027 (m, sh), 1008 (w, sh), 941 (s, sh), 912 (m, shoulder), 901 (s, sh), 885 (m), 860 (w, sh), 839 (m, sh), 828 (m), 738 (s, sh), 732 (m, shoulder), 703 (m, sh), 690 (s), 671 (m, br) cm^{-1}. Mass spectrum (EI, 17 eV; *m/z* (relative intensity)): 410 (3), 326 (100), 283 (14), 139 (12), 138 (64), 123 (44), 121 (16), 91 (17), 79 (10). Anal. Calcd for $C_{18}H_{22}NbO_3P$: C, 52.70; H, 5.40. Found: C, 52.84; H, 5.46.

$Nb(2,4\text{-}C_7H_{11})(CO)_3(PEt_3)$. This compound was prepared from (triethylphosphine)bis(2,4-dimethylpentadienyl)niobium[7] in a manner exactly analogous to that for the dimethylphenylphosphine adduct. Thus, 0.60 g (1.5 mmol) of $Nb(2,4\text{-}C_7H_{11})_2(PEt_3)$in 50 mL of THF was stirred under a CO atmosphere for 3 days, and following an analogous workup, 0.40 g (69% yield, mp 126–128 °C dec) of bright red needles was obtained. ^1H NMR (benzene-d_6, ambient): δ 5.23 (s, 1H, H-3), 3.05 (s, 2H, $H_{1,5\,exo}$), 1.89 (s, 6H, CH_3-Pdl), 1.42 (qn, 6H, J = 7 Hz, P$CH_2$$CH_3$), 0.84 (d of t, 9H, J = 7, 15 Hz, $PCH_2$$CH_3$), 0.77 (d, 2H, J = 3.0 Hz, $H^{1,5}_{endo}$). ^{13}C NMR (benzene-d_6, ambient): δ 262.1 (s, 2C, CO), 249.4 (s, 1C, CO), 122.2 (s, 2C, C-2,4), 89.0 (d, 1C, J = 161.6 Hz, C-3), 65.5 (t, 2C, J = 156.0 Hz, C-1,5), 29.2 (q of m, 2C, J = 127.8 Hz, 6.2 Hz, CH_3-Pdl), 20.9 (d of t, 3C, J = 127.9, 18.0 Hz, $PCH_2$$CH_3$), 7.6 (d of q, 3C, J = 128.0, 4.0 Hz, P$CH_2$$CH_3$). ^{31}P NMR (benzene-d_6, ambient): δ 18.44. IR (Nujol mull): 2920 (vs, br), 1959 (vs, sh), 1863 (vs, br), 1460 (m, br), 1362 (m), 1030 (w, sh), 1010 (vw, sh), 765 (vw, sh), 720 (vw, br) cm^{-1}. Anal. Calcd for $C_{16}H_{26}NbO_3P$: C, 49.24; H, 6.72. Found: C, 49.43; H, 6.80.

$Nb(2,4\text{-}C_7H_{11})(CO)_2(PMe_2Ph)_2$. A 100-mL three-neck flask equipped with a water-cooled reflux condenser, nitrogen inlet, and magnetic stirring bar was charged with 0.50 g of $Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)$ (1.2 mmol) and 50 mL of THF. Dimethylphenylphosphine (0.33 mL, 2.4 mmol) was added via syringe, and the reaction mixture was brought to reflux. Heating was continued for 3 days, during which time the color steadily darkened to brown-red and the IR spectrum indicated no peaks due to the starting material. The THF was removed in vacuo, and the oily residue was extracted with 50 mL of pentane and the extract filtered through a Celite pad under nitrogen. Concentration of the red-brown filtrate to ca. 10 mL and subsequent cooling at −80 °C for 2 days resulted in the formation of a red powder (0.22 g, 36% yield, mp 98–100 °C) that was isolated and dried in vacuo. The powder so isolated was sufficiently pure for elemental analysis and NMR studies; however, single crystals were obtained by the following procedure. The powder was redissolved in 5 mL of pentane and the flask insulated to prevent rapid cooling of the solution. The insulated flask was placed in a −80 °C freezer for 4 days, resulting in several well-formed single crystals that were isolated and dried in vacuo prior to sealing in glass X-ray capillaries under nitrogen. ^1H NMR (toluene-d_8, ambient): δ 7.43–6.99 (m, 10H, $P(C_6H_5)$), 4.77 (s, 1H, H-3), 2.70 (s, 2H, $H_{1,5\,exo}$), 1.64 (d, 6H, $P(CH_3)$, J = 6 Hz), 1.60 (s, 6H, CH_3-Pdl), 0.56 (s, 2H, $H_{1,5\,endo}$). ^{13}C NMR (toluene-d_8, ambient): δ 263.0 (s, 2C, CO), 129.2–128.0 (m, 12C, $P(C_6H_5)$), 116.8 (s, 2C, C-2,4), 94.7 (d, 1C, J = 157.4 Hz, C-3), 66.5 (t, 2C, J = 153.5 Hz, C-1,5), 27.8 (q, 2C, J = 129.5 Hz, CH_3-Pdl), 18.2 (d of q, 4C, J = 127, 24 Hz, $P(CH_3)$). ^{31}P NMR (toluene-d_8, −60 °C): δ 34.98 (s, 1P), 19.31 (s, 1P). IR (Nujol mull): 2935 (vs, br), 2913 (s), 2878 (s), 1865 (s, sh), 1781 (s, br), 1448 (m, br), 1370 (m, sh), 1295 (w, sh), 1280 (w), 1261 (m, sh), 1095 (m, br), 1025 (m, br), 943 (s, sh), 904 (s, sh), 870 (vw), 798 (s, br), 741 (s, sh), 722 (w, sh), 691 (m, sh), 672 (w, sh) cm^{-1}. Anal. Calcd for $C_{25}H_{33}NbO_2P_2$: C, 57.07; H, 8.06. Found: C, 56.74; H, 8.02.

Table I. Crystallographic Data for $Nb(C_7H_{11})(CO)_3(PMe_2Ph)$ and $Nb(C_7H_{11})(CO)_2(PMe_2Ph)_2$

	(a) Crystal Parameters	
formula	$C_{18}H_{22}NbO_3P$	$C_{25}H_{33}NbO_2P_2$
fw	410.3	520.4
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	7.911(5)	11.778(2)
b, Å	10.490(6)	13.966(2)
c, Å	12.829(6)	15.930(3)
α, deg	105.61(4)	
β, deg	95.88(4)	96.33(1)
γ, deg	107.59(4)	
V, Å^3	957.5(8)	2604.5(8)
Z	2	4
cryst dimens, mm	0.25 × 0.30 × 0.32	0.20 × 0.20 × 0.35
cryst color	dark red	dark red
D(calcd), g cm^{-3}	1.42	1.33
μ(Mo Kα), cm^{-1}	7.1	5.9
temp, K	298	298
T(max)/T(min)	1.087	1.045
	(b) Data Collection	
diffractometer	Nicolet R3m	
monochromator	graphite	
radiation	Mo Kα (λ = 0.710 73 Å)	
2θ scan range, deg	4–55	4–52
data collected (hkl)	±11,±14,+17	±15,+18,+20
no. of rflns collected	4670	5643
no. of indpt rflns	4589	5321
no. of indpt obsd rflns, $F_o \geq 5\sigma(F_o)$	3731	3477
std rflns	3 std/197 rflns	3 std/197 rflns
var in stds., %	25.3	<1.5
	(c) Refinement	
$R(F)$, %	3.08	3.69
$R(wF)$, %	3.41	3.89
Δ/σ(max)	0.058	0.056
$\Delta(\rho)$, e Å^{-3}	0.46	0.33
N_o/N_v	13.09	9.17
GOF	0.96	0.97

"$K_2Nb(2,4\text{-}C_7H_{11})(CO)_3$". A 100-mL two-neck flask equipped with a nitrogen inlet and magnetic stirring bar was charged with 0.30 g (0.73 mmol) of $Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)$ and 30 mL of diethyl ether. The addition of 7.15 mL of a 0.204 M solution of potassium naphthalenide in THF via syringe to the red ether solution resulted in the formation of a yellow powder that was washed with two 20-mL portions of ether. The powder was dried in vacuo, resulting in 0.25 g (mp 410 °C dec) of "$K_2Nb(2,4\text{-}C_7H_{11})(CO)_3$" as a pyrophoric tan powder. IR (Nujol mull): 2920 (vs, br), 1756 (s, br), 1690 (vs, br), 1455 (s), 1371 (m), 1150 (w), 1022 (m, br), 764 (w, br), 719 (w, sh) cm^{-1}.

$Nb(2,4\text{-}C_7H_{11})(CO)_4$. A pale yellow suspension of "$K_2Nb(2,4\text{-}C_7H_{11})(CO)_3$" (0.20 g, 0.57 mmol) in 30 mL of 1,2-dimethoxyethane was cooled to −48 °C and placed under an atmosphere of carbon monoxide. The addition of 0.16 g (0.57 mmol) of $HgCl_2$ as a solid to the suspension resulted in an immediate reaction to give a dark gray precipitate and a reddish solution. The reaction mixture was warmed to room temperature and stirred for an additional 6 h, at the end of which time the solvent was removed in vacuo. Extraction of the solid residue with three 50-mL

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Nb(C_7H_{11})(CO)_3(PMe_2Ph)$

	x	*y*	*z*	U^a
Nb	4671.7(3)	1847.0(2)	2798.4(2)	35.2(1)
P	4715(1)	2978.5(7)	1223.9(5)	44.5(3)
C(1)	6915(4)	1574(3)	2220(2)	50(1)
O(1)	8170(3)	1409(3)	1918(2)	81(1)
C(2)	2471(4)	401(3)	1591(2)	51(1)
O(2)	1264(4)	–400(3)	933(2)	87(1)
C(3)	4632(4)	–78(3)	2870(2)	51(1)
O(3)	4595(4)	–1197(3)	2855(2)	80(1)
C(4)	2605(4)	3047(4)	3523(3)	55(1)
C(5)	2903(4)	2276(3)	4199(2)	52(1)
C(6)	4642(4)	2384(3)	4721(2)	53(1)
C(7)	6378(4)	3230(3)	4657(2)	54(1)
C(8)	6681(4)	4147(3)	4042(3)	59(1)
C(9)	1302(6)	1119(5)	4318(4)	78(2)
C(10)	7987(5)	2991(5)	5213(3)	84(2)
C(11)	4902(8)	1930(4)	–108(3)	80(2)
C(12)	2727(5)	3418(4)	869(3)	71(2)
C(13)	6365(3)	5906(2)	2086(2)	58(1)
C(14)	7829	7168	2401	75(2)
C(15)	9510	7166	2163	82(2)
C(16)	9727	5902	1610	85(2)
C(17)	8263	4640	1295	67(2)
C(18)	6582	4642	1533	47(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Nb(C_7H_{11})(CO)_2(PMe_2Ph)_2$

	x	*y*	*z*	U^a
Nb	1977.7(3)	1066.1(2)	2213.3(2)	33.1(1)
P(1)	1139.2(9)	627.6(8)	3581.6(6)	39.7(3)
P(2)	3426(1)	303.2(8)	1320.1(7)	46.2(4)
C(1)	3365(4)	834(3)	3083(3)	51(1)
O(1)	4172(3)	747(3)	3561(2)	88(2)
C(2)	1261(4)	–243(3)	1917(3)	51(1)
O(2)	811(4)	–946(3)	1682(3)	95(2)
C(3)	2818(4)	2625(3)	1934(3)	54(2)
C(4)	1924(4)	2789(3)	2415(3)	46(1)
C(5)	798(4)	2465(3)	2196(3)	43(1)
C(6)	360(4)	1900(3)	1483(3)	51(1)
C(7)	1015(5)	1597(4)	852(3)	58(2)
C(8)	2181(4)	3301(3)	3252(3)	64(2)
C(9)	–864(4)	1575(4)	1454(3)	68(2)
C(10)	1779(4)	1177(4)	4565(3)	67(2)
C(11)	1277(4)	–630(4)	3882(3)	64(2)
C(12)	–754(2)	1722(2)	3949(2)	55(2)
C(13)	–1916	1891	3985	66(2)
C(14)	–2714	1182	3727	66(2)
C(15)	–2350	306	3433	64(2)
C(16)	–1189	137	3397	52(2)
C(17)	–391	846	3655	38(1)
C(18)	2880(4)	–215(4)	302(3)	71(2)
C(19)	4267(6)	–698(4)	1791(4)	83(3)
C(20)	4269(2)	1682(3)	281(2)	61(2)
C(21)	4994	2432	114	87(2)
C(22)	5928	2661	696	100(3)
C(23)	6137	2141	1444	97(3)
C(24)	5412	1391	1611	75(2)
C(25)	4478	1162	1030	49(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Bond Distances and Angles for $Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)$

(a) Bond Distances (Å)			
Nb–C(1)	2.060(3)	Nb–C(8)	2.446(3)
Nb–C(2)	2.078(2)	C(1)–O(1)	1.146(4)
Nb–C(3)	2.037(4)	C(2)–O(2)	1.140(3)
Nb–P	2.602(1)	C(3)–O(3)	1.160(5)
Nb–C(4)	2.459(4)	C(4)–C(5)	1.383(6)
Nb–C(5)	2.419(3)	C(5)–C(6)	1.425(5)
Nb–C(6)	2.383(3)	C(6)–C(7)	1.417(4)
Nb–C(7)	2.431(2)	C(7)–C(8)	1.383(5)
(b) Bond Angles (deg)			
P–Nb–C(1)	78.8(1)	Nb–P–C(11)	116.3(2)
P–Nb–C(2)	76.9(1)	Nb–P–C(12)	115.7(1)
P–Nb–C(3)	134.1(1)	Nb–P–C(18)	113.6(1)
C(1)–Nb–C(2)	105.1(1)	C(11)–P–C(12)	102.2(2)
C(1)–Nb–C(3)	74.5(1)	C(11)–P–C(18)	103.9(2)
C(2)–Nb–C(3)	74.9(1)	C(12)–P–C(18)	103.5(1)
Nb–C(1)–O(1)	178.3(3)	C(4)–C(5)–C(6)	124.7(3)
Nb–C(2)–O(2)	179.5(3)	C(5)–C(6)–C(7)	129.3(3)
Nb–C(3)–O(3)	176.7(3)	C(6)–C(7)–C(8)	124.4(3)

Table V. Selected Bond Distances and Angles for $Nb(2,4\text{-}C_7H_{11})(CO)_2(PMe_2Ph)_2$

(a) Bond Distances (Å)			
Nb–C(1)	2.048(4)	Nb–C(7)	2.448(5)
Nb–C(2)	2.047(4)	C(1)–O(1)	1.157(5)
Nb–P(1)	2.564(1)	C(2)–O(2)	1.158(6)
Nb–P(2)	2.570(1)	C(3)–C(4)	1.388(7)
Nb–C(3)	2.453(4)	C(4)–C(5)	1.409(6)
Nb–C(4)	2.430(4)	C(5)–C(6)	1.432(6)
Nb–C(5)	2.396(4)	C(6)–C(7)	1.398(7)
Nb–C(6)	2.420(4)		
(b) Bond Angles (deg)			
P(1)–Nb–P(2)	135.5(1)	Nb–P(1)–C(10)	117.8(2)
P(1)–Nb–C(1)	75.0(1)	Nb–P(1)–C(11)	115.0(2)
P(1)–Nb–C(2)	78.2(1)	Nb–P(1)–C(17)	119.0(1)
P(2)–Nb–C(1)	77.3(1)	Nb–P(2)–C(18)	117.8(2)
P(2)–Nb–C(2)	77.5(1)	Nb–P(2)–C(19)	116.9(2)
C(1)–Nb–C(2)	107.0(2)	Nb–P(2)–C(25)	112.3(1)
Nb–C(1)–O(1)	176.4(4)	C(10)–P(1)–C(11)	99.3(2)
Nb–C(2)–O(2)	173.8(4)	C(10)–P(1)–C(17)	100.9(2)
C(3)–C(4)–C(5)	124.1(4)	C(11)–P(1)–C(17)	101.7(2)
C(4)–C(5)–C(6)	128.4(4)	C(18)–P(2)–C(19)	100.6(3)
C(5)–C(6)–C(7)	123.9(4)	C(18)–P(2)–C(25)	102.6(2)
		C(19)–P(2)–C(25)	104.8(2)

portions of hexane, followed by filtration of the extracts through Celite, gave a dark orange solution that was concentrated in vacuo to ca. 25 mL and then cooled at –20 °C overnight. Dark orange needles formed during this time, and following removal of the supernatant via syringe and drying in vacuo, 0.12 g (0.040 mmol) of $Nb(2,4\text{-}C_7H_{11})(CO)_4$ was isolated. The yield of the moderately air-sensitive orange needles is 74% (mp 78–81 °C). ^{1}H NMR (toluene-d_8, ambient): δ 4.85 (s, 1H, H-3), 2.80 (s, 2H, $H_{1,5\,exo}$), 1.44 (s, 6H, CH_3-Pdl), 0.64 (s, 2H, $H_{1,5\,endo}$). ^{13}C NMR (toluene-d_8, –90 °C): δ 245.8 (broad s, 4C, CO), 134.0 (s, 2C, C-2,4), 89.9 (d, 1C, J = 164.5 Hz, C-3), 68.6 (t, 2C, J = 157.8 Hz, C-1,5), 28.9 (q, 2C, J = 128.9 Hz, CH_3). IR (Nujol mull): 2920 (vs, br), 2030 (vs, sh), 1967 (s, sh), 1927 (s, sh), 1458 (s, br), 1371 (m), 1150 (vw, br), 1030 (w), 795 (w), 719 (m, sh) cm^{-1}. Anal. Calcd for $C_{11}H_{11}NbO_4$: C, 44.02; H, 3.69. Found: C, 42.21; H, 4.11.

X-ray Crystallography for $Nb(C_7H_{11})(CO)_3(PMe_2Ph)$. A crystal suitable for X-ray structural determination was mounted on a glass fiber with epoxy cement. Crystal, data collection, and refinement parameters are collected in Table I. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Photographic evidence and cell reduction routines indicated $\bar{1}$ Laue symmetry. The chemically sensible results of refinement established the space group as $P\bar{1}$. A semiempirical correction factor for absorption was applied to the data set (216 ψ-scan reflections, T_{max}/T_{min} = 1.087).

The structure was solved by direct methods, which located the Nb atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å, $U = 1.2U$ for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl group was constrained as a rigid ring. Positional parameters are collected in Table II, and selected bond distances and angles are listed in Table IV. All software and the sources of the scattering factors are contained in the SHELXTL (5.1) program library by G. Sheldrick, Siemens XRD Corp., Madison, WI.

X-ray Crystallography for $Nb(C_7H_{11})(CO)_2(PMe_2Ph)_2$. A crystal suitable for X-ray structural determination was mounted on a glass fiber with epoxy cement. Crystal, data collection, and refinement parameters are collected in Table I. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). The systematic absences in the diffraction data uniquely established the space group as $P2_1/c$. A semiempirical correction factor for absorption was applied (216 ψ scans, T_{max}/T_{min} = 1.045).

The structure was solved using a Patterson projection, which located the Nb atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å, $U = 1.2U$ for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl rings were constrained as rigid groups. Positional parameters are collected in Table III, and selected bond distances and angles are listed in Table V. All software and the sources of the scattering factors are contained in the SHELXTL (5.1) program library by G. Sheldrick, Siemens XRD Corp., Madison, WI.

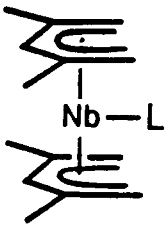
Results and Discussion

As reported earlier, the reaction of $NbCl_4(PEt_3)_2$ with 4 equiv of $K(2,4\text{-}C_7H_{11})$ (C_7H_{11} = dimethylpentadienyl) leads to the spontaneous reduction of Nb(IV) to Nb(II) and isolation of the bright green, 17-electron $Nb(2,4\text{-}C_7H_{11})_2(PEt_3)$[7] (eq 1). More recently, we have found that

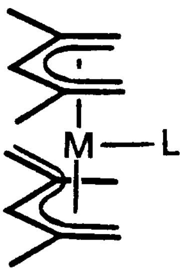
$$NbCl_4(PEt_3)_2 + 4K(2,4\text{-}C_7H_{11}) \rightarrow Nb(2,4\text{-}C_7H_{11})_2(PEt_3) \quad (1)$$

a similar route can be used to prepare $Nb(2,4\text{-}C_7H_{11})_2(PMe_2Ph)$ (eq 2). The PEt_3 complex had been characterized through elemental analysis, magnetic susceptibility (μ = 1.6 μ_B), ESR spectroscopy (A_{Nb} = 120.6 G), and a single-crystal X-ray structural determination, which revealed the expected syn-eclipsed conformation I. This structure is quite typical of related titanium, vanadium, zirconium, and hafnium species,[6,13,14] but differs notably from those for molybdenum and tungsten, which adopt structure II.[6,7] The corresponding PMe_2Ph complex of niobium exhibits an ESR spectrum (A_{Nb} = 120.6 G) similar to that for the PEt_3 complex, and can be expected to adopt the same general structure I.

$$NbCl_4(THF)_2 + PMe_2Ph + 4K(2,4\text{-}C_7H_{11}) \rightarrow Nb(2,4\text{-}C_7H_{11})_2(PMe_2Ph) \quad (2)$$



I

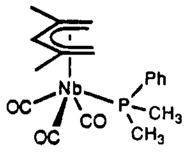


II

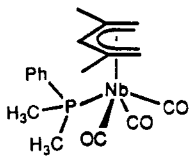
The bright green 17-electron $Nb(2,4\text{-}C_7H_{11})_2(L)$ species react readily with CO, leading to expulsion of one dienyl ligand[15] and the isolation of reddish, 18-electron $Nb(2,4\text{-}C_7H_{11})(CO)_3(L)$ species (eq 3; L = PEt_3, PMe_2Ph). A second PMe_2Ph ligand may be incorporated by a thermally promoted substitution reaction (eq 4). The $Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)$ and $Nb(2,4\text{-}C_7H_{11})(CO)_2(PMe_2Ph)_2$ complexes have been described in an earlier review,[13] and subsequently some $V(C_5H_7)(CO)_3(L)$ and $V(C_5H_7)(CO)_2(L)_2$ analogs have been reported (L = PMe_3, PMe_2Ph).[16] The mono-PEt_3 complex of niobium was initially prepared but on occasion proved difficult to crystallize. The use of L = PMe_2Ph, however, led to much more crystalline compounds which could be readily isolated. The ^1H and ^{13}C NMR spectra of the mono(phosphine) complexes revealed essentially mirror plane symmetry, consistent with either III or IV. Structure III, with the phosphine under the open dienyl edge, appeared more likely, and this was subsequently confirmed by an X-ray structure determination (*vide infra*). For the bis(phosphine) complex, the NMR spectroscopic data revealed equivalence for both the carbonyl and phosphine ligands. As it was expected that the phosphines should be nonequivalent, variable-temperature ^{31}P NMR spectra were obtained (183–298 K), revealing that the single high-temperature resonance at δ 27.1 would undergo decoalescence at ca. 253.0 K, leading to two low-temperature resonances at δ 35.0 and 19.3. These data thereby identify the structure as that in V, with $\Delta G^\ddagger$ = 10.5 ± 0.2 kcal/mol for the dienyl ligand rotation (cf. 10.8 kcal/mol for $V(C_5H_7)(CO)_2(PMe_3)_2$[16]).[17] The structural assignment was also subsequently confirmed by a diffraction study.

$$Nb(2,4\text{-}C_7H_{11})_2(L) + CO(excess) \rightarrow Nb(2,4\text{-}C_7H_{11})(CO)_3(L) \quad (3)$$

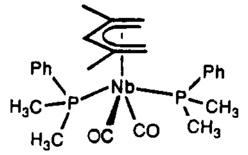
$$Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph) + PMe_2Ph \xrightarrow{\Delta} Nb(2,4\text{-}C_7H_{11})(CO)_2(PMe_2Ph)_2 \quad (4)$$



III



IV



V

Attempts were also made to reduce the monophosphine complex to a dianion, as indicated by eq 5. In fact, a pyrophoric, fairly insoluble product was isolated, which did exhibit the very low C–O stretching frequencies that would be expected for such a species (1690, 1756 cm^{-1})

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(13) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255.

(14) Newbound, T. D.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1992**, *11*, 1693.

(15) The expelled dienyl ligands lead to dimers (tetramethyldecatetraenes), which have been identified by NMR spectroscopy.

(16) Lin, W.-J.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1991**, *10*, 2519.

(17) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

$$\mathrm{Nb(2,4\text{-}C_7H_{11})(CO)_3(L)} + 2e^- \rightarrow \text{“}\mathrm{Nb(2,4\text{-}C_7H_{11})(CO)_3}^{2-}\text{”} \quad (5)$$

and analytical data which are in accord with such a species.[18] While alternative formulations such as $[\mathrm{Nb(C_7H_{11})(CO)_3}]_2^{2-}$, whose neutral isoelectronic molybdenum analog is known,[19] cannot be completely excluded, some indirect evidence that the desired product was present could be obtained through the mild oxidation of the presumed dianion under a CO atmosphere. From this treatment, the complex $\mathrm{Nb(2,4\text{-}C_7H_{11})(CO)_4}$ could be isolated in reasonable yield and characterized through normal methods. Notably, the ^{13}C NMR spectra revealed a single signal for the CO ligands even at −98 °C, indicating a very low barrier to dienyl rotation. Additional attempts to obtain definitive proof of the dianion's formulation through a structural determination were unsuccessful owing to the fact that single crystals of this species could not be obtained, even when additional coordinating ligands (e.g., crown ethers) were added for the alkali-metal ions. Actually, a very small quantity of crystals was isolated, and from a diffraction study, their constitution was revealed to be $\mathrm{K(15\text{-}crown\text{-}5)_2}^+[cis\text{-}\mathrm{Nb(CO)_4(PMe_2Ph)_2}^-]$.[20] Unfortunately, severe disorder in the 15-crown-5 ligands precluded a high-quality structural result. The formation of this compound might well involve expulsion of $\mathrm{K(2,4\text{-}C_7H_{11})}$ from the presumed product $\mathrm{K_2Nb(2,4\text{-}C_7H_{11})(CO)_3}$, initiated either by the presence of $\mathrm{PMe_2Ph}$ in solution from the initial reduction or perhaps by adventitious CO, at least 1 equiv of which had to be scavenged at some point in order to form a tetracarbonyl. The expulsion of cyclopentadienide ion from metal complexes may be brought about under similar circumstances,[21] and even alkylphosphines have been observed to replace the cyclopentadienide ion.[22]

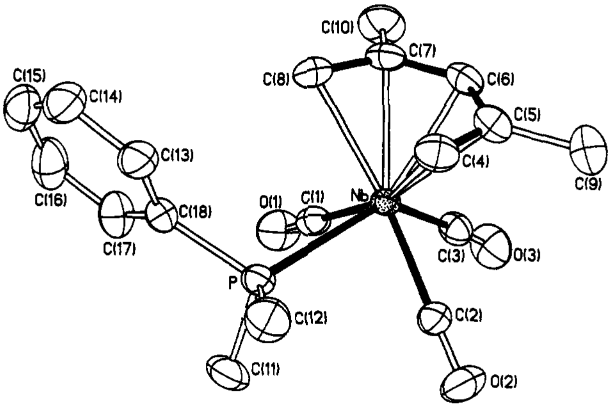

Figure 1. Solid-state structure of $\mathrm{Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)}$.

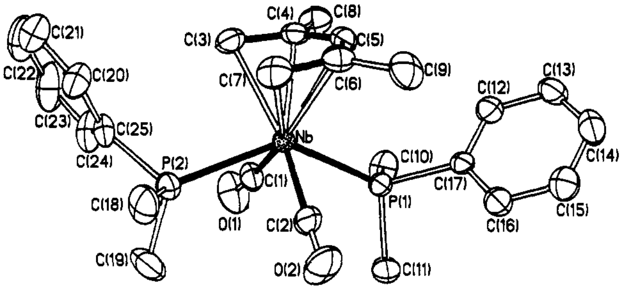

Figure 2. Solid-state structure of $\mathrm{Nb(2,4\text{-}C_7H_{11})(CO)_2(PMe_2Ph)_2}$.

The structures of $\mathrm{Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)}$ (III) and $\mathrm{Nb(2,4\text{-}C_7H_{11})(CO)_2(PMe_2Ph)_2}$ (V) are presented in Figures 1 and 2, with various bonding parameters given in Tables II–V. As can be seen, both complexes adopt the expected piano-stool coordination geometries. However, as has been observed in other $\mathrm{M(pentadienyl)(L)}_x$ (x = 3, 4) complexes, the extent by which the additional x ligands are tilted down is not uniform.[23] Actually, the CO tilts below the Nb center in V average 35.8°, similar to the values in III of 37.1° for its two corresponding carbonyls and 33.3° for its unique carbonyl. The tilt for P(1) in V is also similar, 33.7°. However, the tilts for the phosphine ligands residing below the open dienyl edge are much smaller, being 12.7 and 10.8°, respectively. There is in effect an ca. 22° tilt of these ligands up toward the open dienyl edge, relative to the other ligands. These values may be compared to the tilts for various $\mathrm{M(dienyl)(L)_3}$ complexes, such as $\mathrm{Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)}$ (45.2, 15.5°),[24] $\mathrm{Cr(2,4\text{-}C_7H_{11})(CH_3)(dmpe)}$ (46.3, 15.4°),[25] $\mathrm{Fe(2,4\text{-}C_7H_{11})(I)(CO)_2}$ (43.4, 16.8°),[26] and $\mathrm{Ru(2,4\text{-}C_7H_{11})(CO)(PEt_3)_2}^+$ (44.3, 17.8°),[8] for which the differences in tilts fall in the narrow range of 26.5–30.9°. It can be seen that the tilts in these last four complexes are greater than those in the two niobium species, which may be ascribed to the greater steric crowding in a $\mathrm{M(dienyl)(L)}_x$ complex for x = 4 relative to x = 3. The tilts observed in $\mathrm{Re(2,4\text{-}C_7H_{11})(H)_2(PPh_3)_2}$ (18.9, 57.5°) are even greater[27] and lead to a difference of 32.6°, apparently reflecting significant and dominating dienyl–$\mathrm{PPh_3}$ repulsions, particularly involving the central dienyl carbon atom. In each of these cases, it appears that the upward tilt of the ligand near the open dienyl edge is a result of the presence of unused metal orbital density in that location. One could expect that this should lead to enhanced bonding to the metal for that ligand, and this is indeed clearly observed for the $\mathrm{M(dienyl)(L)_3}$ complexes. For both $\mathrm{Re(2,4\text{-}C_7H_{11})(H)_2(PPh_3)_2}$ and $\mathrm{Nb(2,4\text{-}C_7H_{11})(CO)_2(PPh_3)_2}$, however, just the reverse is observed (2.350(2) vs 2.320(2) Å, 2.570(1) vs 2.564(1) Å; cf. 2.602(1) Å in III), although the magnitudes are smaller than in the $\mathrm{M(dienyl)(L)_3}$ complexes. It has been noted that the unique ligands residing near the open dienyl edge in the $\mathrm{M(dienyl)(L)_3}$ complexes are subject to greater steric crowding than the other L's,[8,28] and the fact that such ligands will be even closer to the open edge in the $\mathrm{M(dienyl)(L)_4}$ analogs would lead to even greater problems and perhaps account for their longer bonds. It is also possible that an electronic effect could be operative, since in the $\mathrm{M(dienyl)(L)_4}$ species the L residing under the

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[18] Anal. Calcd for $\mathrm{C_{10}H_{11}NbO_3K_2}$: C, 34.29; H, 3.17. Found: C, 33.84; H, 2.86.

[19] Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612.

[20] Discrepancy indices of R = 0.077 and R_w = 0.098 could be obtained, but the thermal motion in the crown ethers was so great that the associated bonding parameters were nearly meaningless. The space group is $P\bar{1}$, with a = 9.720(2) Å, b = 14.084(2) Å, c = 17.770(2) Å, α = 93.86(1)°, β = 92.69(1)°, and γ = 92.72(2)° for Z = 2.

[21] Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

[22] Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241.

[23] The sine of the tilt angle is defined as the distance of the substituent below the metal atom position (relative to the dienyl plane) divided by the M–substituent distance.

[24] Newbound, T. D.; Freeman, J. W.; Wilson, D. R.; Kralik, M. S.; Patton, A. T.; Campana, C. F.; Ernst, R. D. *Organometallics* **1987**, *6*, 2432.

[25] Newbound, T. D.; Arif, A. M.; Wilson, D. R.; Rheingold, A. L.; Ernst, R. D. *J. Organomet. Chem.* **1992**, *435*, 73.

[26] Ma, H.; Weber, P.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 854.

[27] Waldman, T. E.; Rheingold, A. L.; Ernst, R. D. *J. Organomet. Chem.* **1991**, *401*, 331.

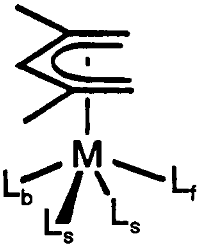
[28] Bleeke, J. R.; Rauscher, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 8972.

central dienyl carbon atom does not have to compete with any ligand situated trans to it.

There also appear to be slight variations in the Nb–CO bonding. The shortest Nb–CO bond seems to occur for Nb–C3 in compound III, for which the CO resides opposite to the phosphine ligand. The Nb–CO bonds for its other two carbonyls are the longest, averaging 2.069(3) Å, while their counterparts in V are significantly closer, at 2.048(3) Å. This is reasonable given the presence of the extra electron-donating phosphine ligand in the latter complex. Overall, the corresponding bond angles involving the CO and PMe_2Ph ligands for the two structures are reasonably similar (Tables IV and V), and the fact that the "cis" angles range from 74.5(1) to 78.8(1)° may be taken as a good indication of significant steric crowding in these compounds.

For the dienyl ligands, one sees the normal shortening for the external vs internal delocalized C–C bonds[29] (1.388(3) vs 1.421(3) Å). The internal C–C(X)–C bond angles are, as usual,[29] somewhat contracted for $X = CH_3$ relative to X = H and average 124.3(2) vs 128.9(3)°, although there may be a slight contraction of both types for V relative to III.[30] Additionally, the methyl groups of the dienyl ligands are tilted toward the metal, as expected, by respective averages of 6.2 vs 4.5°, perhaps again reflecting crowding in the latter compound.[29] The Nb–C bonding patterns in the two complexes are essentially identical, giving average Nb–C(1,5), Nb–C(2,4), and Nb–C(3) bond lengths of 2.451(2), 2.425(2), and 2.389(3) Å, respectively. Notably, the reverse pattern is observed for $Re(2,4\text{-}C_7H_{11})(H)_2(PPh_3)_2$ (2.256(5), 2.274(5), and 2.293(7) Å), which may result from steric interactions between C(3) and the proximate PPh_3 ligand, which experiences a rather large tilt of 57.5° below the rhenium center (*vide supra*). These increased interactions not only are the result of the presence of a larger phosphine ligand but also result from the fact that shorter bonds exist for the Re(III) vs Nb(I) complex.

One can also note that there is significant flexibility in the $M(dienyl)(L)_4$ arrangements. In these species there are three unique ligand (L) positions: front, back, and side (two), as in VI. In the *relatively* uncrowded $Nb(2,4\text{-}C_7H_{11})(CO)_3(PMe_2Ph)$ and $Nb(2,4\text{-}C_7H_{11})(CO)_2(PPh_3)_2$ complexes, one finds respective average L_f–Nb–L_b and L_s–Nb–L_s' angles of ca. 135 and 106°. In the much more crowded $Re(2,4\text{-}C_7H_{11})(H)_2(PPh_3)_2$ structure, the dienyl–PPh_3 interactions force a contraction of the L_f–M–L_b (P–Re–P) angle to 109.6(1)°, and in response the L_s–M–L_s' (H–Re–H) angle opens up to 131(2)°. The relative values of the L_f–M–L_b and L_s–M–L_s' angles have thus been inverted. Quite clearly the actual ligand positions, and the bond angles formed between them, are keenly affected by the relative metal and ligand sizes. Furthermore, it has been noted that the conformational preferences exhibited by edge-bridged pentadienyl (cyclohexadienyl, etc.) complexes may be entirely different from those of the open-edge species.[8,13,28] Recent theoretical treatments on related $M(C_5H_5)L_4$ complexes have revealed a number of similarities in these regards,[31] particularly the fact that there are often different degrees of tilts for the two oppositely positioned pairs of ligands.



VI

Supplementary Material Available: Tables giving additional bond lengths and angles, anisotropic thermal parameters for non-H atoms, and positional parameters for H atoms for $Nb(2,4\text{-}C_7H_{11})(PMe_2Ph)(CO)_3$ and $Nb(2,4\text{-}C_7H_{11})(PMe_2Ph)_2(CO)_2$ (8 pages). Ordering information is given on any current masthead page.

OM930201U

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[29] Ernst, R. D. *Struct. Bonding (Berlin)* **1984**, *57*, 1.

[30] The smaller C–C–C angles for the bis(phosphine) complex allow for the dienyl ligand to back away slightly from the metal. Even smaller C–C–C angles are present in the still more crowded rhenium complex.

[31] (a) Poli, R. *Organometallics* **1990**, *9*, 1892. (b) Lin, Z.; Hall, M. B. *Organometallics* **1993**, *12*, 19.