Pt(diphos)$_2$ as the only complex in solution.

Generation of $Pt(PhCH=CH_2)_3$. A suspension of 1 (50 mg, 105 μmol) in 2 mL of styrene was treated with Ph_3SiH (55 mg, 211 μmol). Stirring for 30 min affords a clear yellow solution. ^{195}Pt NMR spectroscopy shows $Pt(PhCH=CH_2)_3$ both under N_2 and in air. The synthesis can be accomplished under N_2 by using $MeCl_2SiH$ as reducing agent.

The Pt(0) styrene is separated from silane as follows: 2 mL of the styrene solution was stirred together with 2 mL of H_2O and 0.5 ml concentrated NH_3 for ca. 75 min. If the phases do not separate cleanly, an additional 2 mL of water may be added. The styrene phase was separated and stirred with another 2 mL of H_2O for 20 min. Separation of the styrene phase was followed by placing it on a 5-mm wide column containing 3.5 cm of basic Alox (activity I). After the solution was collected, the column was washed with 1.5 mL of styrene and this eluate added to the first fraction. Omitting the NH_3 treatment results in reduced yields and requires a longer column, ca. 7 cm with 2.5 cm diameter. $[Pt(PhCH=CH_2)_3]$ (isomers A and B): ^{195}Pt NMR (δ, CD_2Cl_2/styrene (15:1), 263 K) –5892 (A), –5873 (B); ^{195}Pt NMR (δ, CD_2Cl_2/styrene (50:1), 193 K) –5921 (A), –5958 (B); ^{195}Pt NMR (δ, toluene-d_8/styrene (1:10), 263 K), –5904 (A), –5886 (B); ^{195}Pt NMR (δ, toluene-d_8/styrene (7:1), 263 K) –5902 (A), –5882 (B); ^{195}Pt NMR (δ, toluene-d_8/styrene (7:1), 223 K) –5930 (A), –5958 (B).

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Registry No. **1**, 106862-48-0; **2**, 106799-82-0; **3**, 12012-50-9; **6**, 59982-20-6; **7**, 113948-64-4; **8**, 59982-22-8; $PtCl_2$(1,5-COD), 12080-32-9; *cis*-$[PtCl_2(PhCN)(PhCH=CH_2)]$, 113948-65-5; *cis*-$[PtCl_2(PhCH=CH_2)(p\text{-}MeOC_6H_4CN)]$, 113948-66-6; Pt(diphos)$_2$, 25398-76-9; *cis*-$[PtCl_2(p\text{-}MeC_6H_4CH=CH_2)_2]$, 113948-67-7; *cis*-$[PtCl_2(PhNH_2)_2]$, 41637-08-5; *cis*-$[PtCl_2(PPh_3)_2]$, 15604-36-1; *cis*-$[PtCl_2\{P(OPh)_3\}_2]$, 30053-58-8; $PhCH=CH_2$, 100-42-5; $CH_2=CHOEt$, 109-92-2; $CH_2=CHSiMe_3$, 754-05-2; $CH_2=CH(CH_2)_3CH_3$, 592-41-6; $CH_2=C(CH_3)Ph$, 300-57-2; $HC\equiv CPr$, 627-19-0; $HC\equiv CPh$, 536-74-3; $MeCl_2SiH$, 75-54-7; Me_2ClSiH, 1066-35-9; Et_2MeSiH, 760-32-7; Ph_2MeSiH, 776-76-1; $(PhCH_2)_3SiH$, 1747-92-8; Ph_3SiH, 789-25-3; $PhMe_2SiH$, 766-77-8; Et_3SiH, 617-86-7; $PhCH_2CH_2SiCl_2Me$, 772-65-6; $PhCH(CH_3)CH_2SiCl_2Me$, 13617-28-2; $PhCH_2CH_2SiClMe_2$, 17146-08-6; $PhCH(CH_3)SiClMe_2$, 65118-86-7; $PhCH_2CH_2SiMeEt_2$, 76111-01-8; $PhCH_2CH_2SiMe_2Ph$, 62257-76-5; $PhCH(CH_3)SiMe_2Ph$, 65231-38-1; $PhCH_2CH_2Si(CH_2Ph)_3$, 113948-54-2; $PhCH(CH_3)Si(CH_2Ph)_3$, 113948-55-3; *trans*-$PhCH=CHSi(CH_2Ph)_3$, 113948-56-4; $PhCH_2CH_3$, 100-41-4; $PhMe_2SiCH_2CH_2OEt$, 113948-57-5; $Ph_3SiCH_2CH_2SiMe_3$, 102105-77-1; $PhMe_2Si(CH_2)_5CH_3$, 65118-84-5; *trans*-$PhMe_2SiCH=CHPr$, 113948-58-6; $CH_2=C(SiMe_2Ph)Pr$, 113948-59-7; *trans*-$PhMe_2SiCH=CHPh$, 64788-85-8; $CH_2=C(SiMe_2Ph)Ph$, 63935-90-0; *trans*-$Et_3SiCH=CHPh$, 21209-32-5; $CH_2=C(SiEt_3)Ph$, 42478-41-1; $PhCOCH_3$, 98-86-2; PhCHO, 100-52-7; CH_3COCH_3, 67-64-1; $CH_3COCH_2CH_3$, 78-93-3; CH_3CO-*i*-Bu, 108-10-1; NEt_3, 121-44-8; $PhNH_2$, 62-53-3; PPh_3, 603-35-0; $AsPh_3$, 603-32-7; $SbPh_3$, 603-36-1; $PhCH(CH_3)OSiCl_2Me$, 60199-01-1; $PhCH_2OSiCl_2Me$, 113948-61-1; $(CH_2)_4CHOSiMe_2Cl$, 113948-62-2; $(CH_3)_2CHOSiMeCl_2$, 999-89-3; $CH_3CH_2CH(CH_3)OSiMeCl_2$, 1825-79-2; *i*-$BuCH(CH_3)OSiMeCl_2$, 113948-63-3; $PhMe_2SiOMe$, 17881-88-8; $PhMe_2SiOEt$, 1825-58-7; $PhMe_2SiOCH(CH_3)_2$, 17988-21-5; $PhMe_2SiOCH(CH_2)_5$, 65335-82-2; Et_3SiOMe, 2117-34-2; Et_3SiOEt, 597-67-1; $Et_3SiOCH(CH_3)_2$, 1571-45-5; $Et_3SiOCH(CH_2)_5$, 4419-18-5; indene, 95-13-6; 2-vinylpyridine, 100-69-6; 1-(dimethylphenylsilyl)indan, 41273-54-5; 1-triethylsilyl-1-(2-pyridinyl)ethane, 113948-60-0; 1-triethylsilyl-2-(2-pyridinyl)ethane, 17082-72-3; cyclopentanone, 120-92-3; pyridine, 110-86-1; 2-ethylpyridine, 100-71-0; 4-methylpyridine, 108-89-4; 4-hydroxypyridine, 626-64-2; 4-acetylpyridine, 1122-54-9; 4-aminopyridine, 504-24-5; 4-methylbenzenamine, 106-49-0; 1,2-phenylenediamine, 95-54-5; piperidine, 110-86-1.

Isolation and X-ray Crystal Structures of the Homoleptic, σ-Bonded, Transition-Metal Aryl Complexes $[(LiEt_2O)_4VPh_6]$ and $[(LiEt_2O)_3CrPh_6]$

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The isolation and X-ray crystal structures of the homoleptic, σ-bonded, transition-metal aryl complexes $[(LiEt_2O)_4VPh_6]$ (1) and $[(LiEt_2O)_3CrPh_6]$ (2) are reported. In both compounds the transition metal is surrounded by six, octahedrally disposed, phenyl groups. In 1, four ether-solvated Li^+ ions cap alternate faces of the VC_6 octahedron, giving rise to a tetrahedral array of four Li^+ ions with V at the center. In 2, one of the $(LiEt_2O)$ moieties is absent so that the $CrLi_3$ group is in an array of C_{3v} symmetry. Both complexes feature long M–C bonds and fairly short M–Li distances, suggesting the possibility of significant M–Li interaction. Crystal data, with Mo Kα (λ = 0.71069 Å) radiation, at 130 K are as follows: 1, a = 12.790 (3) Å, b = 14.352 (4) Å, c = 13.117 (3) Å, β = 95.06 (2)°, Z = 2, space group $P2_1$, R = 0.036; 2, a = 12.010 (3) Å, b = 19.148 (8) Å, c = 20.410 (7) Å, α = 113.91 (2)°, β = 95.51 (3)°, γ = 90.32 (3)°, Z = 4, space group $P\bar{1}$, R = 0.049.

Introduction

The σ-bonded metal alkyls and aryls constitute a major class of transition-metal organometallics.[1,2] An interesting but barely known sub-class of these compounds involves low-oxidation state (<+2), electron-rich, polyphenyl derivatives, which contain no π-acceptor ligands and are generally obtained as complexes with ether-solvated alkali-metal ions. A notable feature of these compounds is the possibility of a σ-acceptor interaction of the lithium ions with the central transition-metal atom as suggested by Taube.[3] Such interactions have been reported in a

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number of Li-Ni/olefin complexes,[4,5] but information for Li/phenyl/transition-metal complexes is very scarce owing to the almost complete absence of X-ray data. A rare exception is the species [(LiEt$_2$O)$_4$FePh$_4$][6] which has a short Li–Fe distance of 2.50 (1) Å, which is less than the sum (2.59 Å) of the covalent radii of these elements. There have also been a number of publications concernining reactions of the halides of the earlier transition metals with an excess of PhLi in ethers. Examples include [VPh$_2$·(LiPh)$_4$·3.5Et$_2$O],[7] VBz$_2$·2LiBz·THF,[8] [MPh$_2$·(LiPh)$_4$·3.5Et$_2$O][9,10] (M = Nb, Ta), Li$_2$CrR$_4$,[11] [Mo(C$_6$H$_4$)(PhLi·OEt$_2$)$_4$],[12] and [WPh$_2$(LiPh·Et$_2$O$_4$].[13] However, no X-ray crystal structures have been reported for any of these complexes.

We recently described the structures of two complexes from the treatment of MCl$_5$ (M = Nb or Ta)[14] with excess PhLi in THF. These involved two benzyne and either three or four Ph groups in the coordination sphere with the metals in the oxidation states III for Nb and V for Ta. We now report the isolation and X-ray crystal structures of two, first-row, metal complexes, [(LiEt$_2$O)$_4$VPh$_6$] (1) and [(LiEt$_2$O)$_3$CrPh$_6$] (2). So far as we are aware 1 is the first structure of a mononuclear, homoleptic, σ-bonded V(II) organometallic. Its electronically similar chromium analogue, [(LiEt$_2$O)$_3$CrPh$_6$] (2), although of less novelty, also has interesting structural features. In addition, it is of historical interest since it has been described as the "first real organochromium compound".[15,16]

Experimental Section

All manipulations were carried out under an N$_2$ atmosphere by using standard Schlenk tube techniques. All solvents were distilled from drying agents and degassed three times immediately before use. VCl$_3$, CrCl$_2$, and CrCl$_3$ were purchased from Cerac and used as received. Halide-free PhLi was freshly synthesized from PhI and *n*-BuLi.[17] UV–visible spectra were recorded on a Hewlett-Packard 8450A UV–visible spectrometer. Both compounds 1 and 2 gave satisfactory C and H analyses.

Tetrakis(lithium ethereate)hexaphenylvanadium(II) (1). This synthesis is a modification of that reported, but not described in detail, by Kurras.[7] Vanadium trichloride (0.615 g, 3.9 mmol) was added by solid-addition tube to an ether (60 mL) solution of phenyllithium (2.3 g, 27.4 mmol), cooled in a dry ice/acetone bath. The dark green solution was stirred for 1 h and allowed to warm to ambient temperature overnight. The deep purple solution was then filtered and the volume reduced to ~40 mL. Cooling to ca. 5 °C in the refrigerator afforded the product 1 as large purple crystals: yield 1.42 g, 43%; mp 100 °C dec.

Table I. Crystal Data and Data Collection Parameters for 1 and 2

	1	2
formula	$C_{52}H_{70}O_4VLi_4$	$C_{4,}H_{60}O_3CrLi_3$
fw	837.84	757.83
color and habit	dark purple prisms	yellow-orange prisms
cryst system	monoclinic	triclinic
space group	$P2_1$	$P\bar{1}$
a, Å	12.790 (3)	12.010 (3)
b, Å	14.352 (4)	19.148 (8)
c, Å	13.117 (3)	20.410 (7)
α, deg		113.91 (2)
β, deg	95.06 (2)	95.51 (3)
γ, deg		90.32 (3)
V, Å^3	2398 (1)	4266 (2)
T, K	130	130
Z	2	4
cryst dimens, mm	0.35 × 0.40 × 0.50	0.8 × 0.73 × 0.85
d(calcd), g cm^{-3}	1.16	1.18
μ(Mo Kα), cm^{-1}	2.5	3.0
range of abs fctrs	1.08–1.14	1.20–1.79
scan speed, deg min^{-1}	15	60
scan width, deg	0.9	1.0
w offset for bkgd, deg	0.9	1.0
2θ range, deg.	0–50	0–50
octants collected	$+h, +k, \pm l$	$+h, \pm k, \pm l$
no. of data collected	4371	15111
no. of unique data	4214	14953
R(merge)	0.008	0.010
no. of data used in refnmt	4164, $I > 2\sigma(I)$	10489, $I > 3\sigma(I)$
no. of parameters refnd	565	1009
data/variable ratio	7.4	10.2
$R(F)$	0.036	0.049
$R_w(F)$	0.039	0.054
weighting scheme	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o)]^{-1}$
largest Δ/σ	0.022 for rotation of H on C(37)	0.006 for y of Li(6)
largest feature on final diff map, e Å^{-3}	0.41	0.63, 1.00 Å from C(94)

Tris(lithium etherate)hexaphenylchromium (III). The procedure was very similar to that employed for vanadium. Addition of chromium dichloride (0.37 g, 3 mmol) to phenyllithium (1.765 g, 21 mmol) in Et$_2$O (60 mL) affords a golden brown solution with some greenish precipitate. After filtration, a slight reduction (5–10 mL) in volume under reduced pressure results in the appearance of orange crystals on the walls of the Schlenk tube. Rewarming to ambient temperature followed by cooling in the refrigerator gave the product 2 as large orange crystals: yield 0.91 g, 40%; 110 °C dec.

X-ray Crystallographic Studies

Structure Determination and Refinement. Crystals of the title compounds were coated with hydrocarbon oil to retard decomposition and mounted in the cold stream of a Syntex P2$_1$ diffractometer equipped with a locally modified LT-1 low-temperature device. No decay in the intensity of standard reflections was observed during data collection. Solution of the structures was accomplished by using the Patterson technique. All crystallographic computing was carried out using SHELXTL version 5 programs, installed on a Data General Eclipse computer. Atomic scattering factors and anomalous dispersion corrections were from common sources.[18] For 1 systematic absences indicate a choice of space groups, $P2_1$ or $P2_1/m$. The latter was ruled out by the lack of a mirror plane in the molecule and by successful refinement in $P2_1$. The handedness was not determined. For 2, no higher symmetry cell could be found by using our cell reduction program.

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Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	*y*	*z*	*U*^{a}		*x*	*y*	*z*	*U*^{a}
					Compound 1				
V	2300 (1)	2000	2499 (1)	17 (1)*	C(33)	−914 (3)	3582 (2)	1756 (2)	28 (1)*
C(1)	2386 (2)	2534 (2)	808 (2)	21 (1)*	C(34)	−1566 (3)	3263 (2)	2464 (3)	30 (1)*
C(2)	2410 (2)	1928 (2)	−49 (2)	22 (1)*	C(35)	−1180 (2)	2606 (2)	3166 (2)	29 (1)*
C(3)	2469 (2)	2227 (2)	−1053 (2)	27 (1)*	C(36)	−151 (2)	2281 (2)	3165 (2)	26 (1)*
C(4)	2527 (2)	3166 (2)	−1275 (2)	26 (1)*	C(37)	5645 (4)	5299 (3)	1578 (4)	59 (2)*
C(5)	2515 (2)	3796 (2)	−474 (2)	25 (1)*	C(38)	4759 (3)	4650 (3)	1233 (3)	36 (1)*
C(6)	2423 (2)	3484 (2)	514 (2)	22 (1)*	O(1)	5028 (2)	3679 (2)	1408 (2)	30 (1)*
C(7)	1655 (2)	571 (2)	1893 (2)	20 (1)*	C(39)	5771 (3)	3309 (3)	752 (3)	36 (1)*
C(8)	626 (2)	247 (2)	2028 (2)	23 (1)*	C(40)	5278 (3)	3081 (3)	−298 (3)	47 (1)*
C(9)	225 (3)	−611 (2)	1685 (2)	27 (1)*	C(41)	5188 (3)	−1676 (3)	3354 (3)	51 (1)*
C(10)	845 (3)	−1220 (2)	1173 (2)	30 (1)*	C(42)	4268 (3)	−1141 (3)	2884 (3)	35 (1)*
C(11)	1857 (3)	−945 (2)	1021 (2)	28 (1)*	O(2)	3569 (2)	−806 (2)	3604 (2)	37 (1)*
C(12)	2232 (2)	−83 (2)	1365 (2)	23 (1)*	C(43A)	3205 (4)	−1436 (4)	4344 (4)	33 (1)
C(13)	4030 (2)	1465 (2)	2510 (2)	22 (1)*	C(44A)	2470 (6)	−2130 (6)	3770 (5)	53 (2)
C(14)	4505 (2)	1228 (2)	1602 (2)	23 (1)*	C(43B)	2789 (7)	−1587 (7)	3748 (7)	39 (3)
C(15)	5528 (3)	905 (3)	1580 (3)	31 (1)*	C(44B)	3101 (10)	−1966 (10)	4828 (10)	63 (4)
C(16)	6165 (3)	785 (3)	2481 (3)	39 (1)*	C(45)	−82 (3)	1032 (3)	−1725 (3)	36 (1)*
C(17)	5750 (3)	995 (3)	3396 (3)	34 (1)*	C(46)	−83 (3)	683 (2)	−642 (2)	28 (1)*
C(18)	4724 (2)	1319 (2)	3399 (2)	26 (1)*	O(3)	−330 (2)	1433 (2)	31 (2)	25 (1)*
C(19)	2240 (2)	1483 (2)	4189 (2)	21 (1)*	C(47)	−1354 (3)	1350 (3)	407 (3)	33 (1)*
C(20)	2859 (2)	1840 (2)	5049 (2)	23 (1)*	C(48)	−2241 (3)	1403 (3)	−427 (3)	39 (1)*
C(21)	2870 (3)	1484 (2)	6040 (2)	30 (1)*	C(49)	1408 (3)	5296 (3)	5505 (4)	53 (1)*
C(22)	2260 (3)	723 (3)	6243 (2)	31 (1)*	C(50)	1846 (3)	4332 (3)	5548 (3)	35 (1)*
C(23)	1618 (2)	342 (2)	5443 (2)	26 (1)*	O(4)	1118 (2)	3672 (2)	5083 (2)	34 (1)*
C(24)	1619 (2)	710 (2)	4461 (2)	23 (1)*	C(51A)	190 (3)	3458 (3)	5605 (3)	30 (1)
C(25)	2928 (2)	3480 (2)	3108 (2)	19 (1)*	C(52A)	416 (5)	2609 (4)	6263 (4)	39 (2)
C(26)	3941 (3)	3625 (2)	3629 (2)	25 (1)*	C(51B)	605 (14)	3370 (11)	6033 (14)	33 (5)
C(27)	4343 (3)	4499 (3)	3926 (2)	32 (1)*	C(52B)	−3 (14)	2498 (12)	5868 (14)	34 (5)
C(28)	3751 (3)	5292 (3)	3731 (3)	36 (1)*	Li(1)	3906 (4)	2916 (4)	1852 (4)	29 (2)*
C(29)	2748 (3)	5209 (2)	3242 (2)	32 (1)*	Li(2)	2965 (4)	398 (4)	3232 (4)	27 (2)*
C(30)	2369 (3)	4324 (2)	2949 (2)	25 (1)*	Li(3)	822 (4)	1797 (3)	1017 (4)	25 (2)*
C(31)	573 (2)	2585 (2)	2470 (2)	21 (1)*	Li(4)	1557 (4)	2955 (4)	3963 (4)	30 (2)*
C(32)	115 (2)	3252 (2)	1765 (2)	23 (1)*					
					Compound 2				
Cr(1)	3060 (1)	6021 (1)	2539 (1)	15 (1)*	C(28)	5509 (3)	8471 (2)	3193 (2)	33 (2)*
Cr(2)	7708 (1)	1027 (1)	2366 (1)	15 (1)*	C(29)	4480 (3)	8455 (2)	3449 (2)	29 (1)*
Li(1)	5112 (4)	6172 (3)	3030 (3)	24 (2)*	C(30)	3870 (3)	7772 (2)	3242 (2)	24 (1)*
Li(2)	2973 (5)	4951 (3)	1028 (3)	25 (2)*	C(31)	1919 (3)	4950 (i)	1926 (2)	19 (1)*
Li(3)	1574 (4)	5662 (3)	3087 (3)	24 (2)*	C(32)	737 (3)	4965 (2)	1811 (2)	21 (1)*
Li(4)	5877 (4)	1166 (3)	3030 (3)	25 (2)*	C(33)	8 (3)	4325 (2)	1563 (2)	26 (1)*
Li(5)	9427 (5)	649 (3)	3069 (3)	26 (2)*	C(34)	425 (3)	3607 (2)	1399 (2)	29 (1)*
Li(6)	7367 (5)	−31 (3)	1023 (3)	26 (2)*	C(35)	1568 (3)	3546 (2)	1490 (2)	27 (1)*
O(1)	6528 (2)	6211 (1)	3564 (1)	25 (1)*	C(36)	2291 (3)	4197 (2)	1747 (2)	22 (1)*
O(2)	2875 (2)	4058 (1)	143 (1)	25 (1)*	C(37)	7592 (3)	861 (2)	3392 (2)	19 (1)*
O(3)	613 (2)	5307 (1)	3596 (1)	26 (1)*	C(38)	7732 (3)	163 (2)	3469 (2)	22 (1)*
O(4)	4648 (2)	1254 (1)	3580 (1)	29 (1)*	C(39)	7708 (3)	88 (2)	4116 (2)	28 (1)*
O(5)	10605 (2)	255 (1)	3497 (1)	30 (1)*	C(40)	7523 (3)	705 (2)	4735 (2)	32 (2)*
O(6)	7162 (2)	−927 (1)	133 (1)	25 (1)*	C(41)	7361 (3)	1408 (2)	4697 (2)	29 (1)*
C(1)	3504 (3)	5865 (2)	3394 (2)	19 (1)*	C(42)	7399 (3)	1476 (2)	4051 (2)	22 (1)*
C(2)	3898 (3)	6488 (2)	4054 (2)	22 (1)*	C(43)	8692 (3)	−41 (2)	1921 (2)	20 (1)*
C(3)	4171 (3)	6419 (2)	4698 (2)	26 (1)*	C(44)	8255 (3)	−794 (2)	1736 (2)	23 (1)*
C(4)	4077 (3)	5711 (2)	4728 (2)	28 (1)*	C(45)	8873 (3)	−1440 (2)	1461 (2)	29 (1)*
C(5)	3703 (3)	5086 (2)	4110 (2)	26 (1)*	C(46)	9994 (3)	−1383 (2)	1363 (2)	31 (1)*
C(6)	3424 (3)	5166 (2)	3468 (2)	21 (1)*	C(47)	10467 (3)	−665 (2)	1530 (2)	27 (1)*
C(7)	1626 (3)	6719 (2)	2836 (2)	20 (1)*	C(48)	9832 (3)	−20 (2)	1799 (2)	22 (1)*
C(8)	1407 (3)	7001 (2)	3561 (2)	22 (1)*	C(49)	7876 (3)	1217 (2)	1379 (2)	19 (1)*
C(9)	542 (3)	7477 (2)	3848 (2)	26 (1)*	C(50)	8563 (3)	815 (2)	830 (2)	22 (1)*
C(10)	−172 (3)	7704 (2)	3407 (2)	28 (1)*	C(51)	8770 (3)	1023 (2)	275 (2)	24 (1)*
C(11)	2 (3)	7450 (2)	2690 (2)	27 (1)*	C(52)	8316 (3)	1661 (2)	230 (2)	28 (1)*
C(12)	868 (3)	6975 (2)	2418 (2)	22 (1)*	C(53)	7630 (3)	2079 (2)	747 (2)	28 (1)*
C(13)	2582 (3)	6192 (2)	1357 (2)	19 (1)*	C(54)	7412 (3)	1858 (2)	1296 (2)	24 (1)*
C(14)	3025 (3)	6832 (2)	1274 (2)	23 (1)*	C(55)	6683 (3)	2047 (2)	2766 (2)	19 (1)*
C(15)	2625 (3)	7049 (2)	727 (2)	28 (1)*	C(56)	7187 (3)	2764 (2)	3238 (2)	22 (1)*
C(16)	1766 (3)	6628 (2)	215 (2)	27 (1)*	C(57)	6647 (3)	3448 (2)	3427 (2)	27 (1)*
C(17)	1320 (3)	5987 (2)	255 (2)	25 (1)*	C(58)	5548 (3)	3459 (2)	3160 (2)	28 (1)*
C(18)	1716 (3)	5779 (2)	810 (2)	22 (1)*	C(59)	5010 (3)	2775 (2)	2700 (2)	28 (1)*
C(19)	4496 (3)	5308 (2)	1858 (2)	19 (1)*	C(60)	5561 (3)	2097 (2)	2515 (2)	24 (1)*
C(20)	4950 (3)	5351 (2)	1259 (2)	23 (1)*	C(61)	6111 (3)	306 (2)	1859 (2)	20 (1)*
C(21)	5822 (3)	4926 (2)	927 (2)	28 (1)*	C(62)	5636 (3)	−217 (2)	2091 (2)	23 (1)*
C(22)	6318 (3)	4420 (2)	1179 (2)	31 (1)*	C(63)	4641 (3)	−647 (2)	1773 (2)	29 (1)*
C(23)	5921 (3)	4347 (2)	1763 (2)	27 (1)*	C(64)	4054 (3)	−583 (2)	1178 (2)	32 (1)*
C(24)	5042 (3)	4779 (2)	2091 (2)	22 (1)*	C(65)	4476 (3)	−82 (2)	920 (2)	29 (1)*
C(25)	4223 (3)	7054 (2)	2769 (2)	19 (1)*	C(66)	5468 (3)	346 (2)	1255 (2)	22 (1)*
C(26)	5269 (3)	7105 (2)	2534 (2)	25 (1)*	C(67)	9294 (3)	1735 (2)	2880 (2)	20 (1)*
C(27)	5904 (3)	7792 (2)	2739 (2)	30 (1)*	C(68)	9954 (3)	2000 (2)	2476 (2)	25 (1)*

Table II (Continued)

	x	y	z	U^a		x	y	z	U^a
C(69)	10903 (3)	2491 (2)	2778 (2)	28 (1)*	C(83)	−670 (3)	4176 (2)	3199 (2)	39 (2)*
C(70)	11270 (3)	2751 (2)	3506 (2)	29 (1)*	C(84)	1084 (4)	5877 (3)	4897 (2)	54 (2)*
C(71)	10672 (3)	2507 (2)	3927 (2)	26 (1)*	C(85)	4557 (3)	727 (3)	3922 (2)	38 (2)*
C(72)	9720 (3)	2020 (2)	3613 (2)	24 (1)*	C(86)	3594 (3)	1566 (2)	3443 (2)	33 (2)*
C(73)	6672 (3)	5651 (2)	3861 (2)	28 (1)*	C(87)	4406 (4)	1149 (4)	4723 (3)	65 (3)*
C(74)	7556 (3)	6508 (2)	3434 (2)	29 (1)*	C(88)	2910 (3)	995 (2)	2762 (2)	41 (2)*
C(75)	7099 (3)	5994 (3)	4649 (2)	38 (2)*	C(89)	10615 (3)	−554 (2)	3336 (2)	32 (1)*
C(76)	8006 (4)	5972 (2)	2765 (2)	43 (2)*	C(90)	11317 (3)	741 (2)	4135 (2)	35 (2)*
C(77)	1790 (3)	3754 (2)	−248 (2)	40 (2)*	C(91)	11740 (3)	−879 (2)	3115 (2)	42 (2)*
C(78)	3649 (3)	3482 (2)	131 (2)	32 (1)*	C(92)	10732 (4)	879 (3)	4794 (3)	55 (2)*
C(79)	1634 (4)	3877 (3)	−927 (2)	54 (2)*	C(93)	6387 (3)	−1509 (2)	136 (2)	31 (1)*
C(80)	4077 (4)	3071 (2)	−591 (2)	44 (2)*	C(94)	8124 (3)	−1233 (2)	−252 (2)	37 (2)*
C(81)	519 (3)	4495 (2)	3401 (2)	29 (1)*	C(95)	5710 (4)	−1929 (2)	−606 (2)	45 (2)*
C(82)	236 (3)	5770 (2)	4286 (2)	30 (1)*	C(96)	8051 (4)	−1118 (3)	−950 (2)	51 (2)*

[a] Parameters with an asterisk are equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

Compound 1			
Bond Lengths			
V–C(1)	2.359 (3)	V–C(7)	2.325 (3)
V–C(13)	2.342 (3)	V–C(19)	2.344 (3)
V–C(25)	2.383 (3)	V–C(31)	2.360 (3)
V···Li(1)	2.642 (5)	V···Li(2)	2.606 (5)
V···Li(3)	2.606 (5)	V···Li(4)	2.606 (6)
Li(1)–C(1)	2.342 (6)	Li(1)–C(13)	2.255 (6)
Li(1)–C(25)	2.302 (6)	Li(2)–C(7)	2.331 (6)
Li(2)–C(13)	2.307 (6)	Li(2)–C(19)	2.252 (6)
Li(3)–C(1)	2.301 (6)	Li(3)–C(7)	2.311 (6)
Li(3)–C(31)	2.263 (6)	Li(4)–C(19)	2.295 (6)
Li(4)–C(25)	2.291 (6)	Li(4)–C(31)	2.296 (6)
Bond Angles			
C(1)–V–C(7)	90.6 (1)	C(1)–V–C(13)	89.4 (1)
C(1)–V–C(19)	179.0 (1)	C(1)–V–C(25)	89.0 (1)
C(1)–V–C(31)	89.4 (1)	C(7)–V–C(13)	91.1 (1)
C(7)–V–C(19)	90.2 (1)	C(7)–V–C(25)	178.9 (1)
C(7)–V–C(31)	90.3 (1)	C(13)–V–C(19)	90.0 (1)
C(13)–V–C(25)	90.0 (1)	C(13)–V–C(31)	178.2 (1)
C(19)–V–C(25)	90.2 (1)	C(19)–V–C(31)	91.1 (1)
C(25)–V–C(31)	88.6 (1)	Li(1)–V–Li(2)	108.6 (2)
Li(1)–V–Li(3)	110.4 (2)	Li(1)–V–Li(4)	108.6 (2)
Li(2)–V–Li(3)	111.6 (2)	Li(2)–V–Li(4)	108.7 (2)
Li(3)–V–Li(4)	108.7 (2)		
Compound 2			
Bond Lengths			
Cr(1)–C(1)	2.266 (4)	Cr(1)–C(7)	2.234 (3)
Cr(1)–C(13)	2.222 (4)	Cr(1)–C(19)	2.262 (3)
Cr(1)–C(25)	2.229 (3)	Cr(1)–C(31)	2.266 (3)
Cr(1)···Li(1)	2.656 (5)	Cr(1)···Li(2)	2.649 (5)
Cr(1)···Li(3)	2.681 (7)	Li(1)–C(1)	2.290 (7)
Li(1)–C(19)	2.334 (6)	Li(1)–C(25)	2.216 (8)
Li(2)–C(13)	2.257 (7)	Li(2)–C(19)	2.265 (6)
Li(2)–C(31)	2.327 (7)	Li(3)–C(1)	2.331 (6)
Li(3)–C(7)	2.281 (8)	Li(3)–C(31)	2.284 (6)
Bond Angles			
C(1)–Cr(1)–C(7)	90.0 (1)	C(1)–Cr(1)–C(13)	178.3 (1)
C(1)–Cr(1)–C(19)	90.9 (1)	C(1)–Cr(1)–C(25)	90.0 (1)
C(1)–Cr(1)–C(31)	90.1 (1)	C(7)–Cr(1)–C(13)	88.4 (1)
C(7)–Cr(1)–C(19)	179.0 (1)	C(7)–Cr(1)–C(25)	91.9 (1)
C(7)–Cr(1)–C(31)	89.8 (1)	C(13)–Cr(1)–C(19)	90.7 (1)
C(13)–Cr(1)–C(25)	90.2 (1)	C(13)–Cr(1)–C(31)	89.8 (1)
C(19)–Cr(1)–C(25)	88.6 (1)	C(19)–Cr(1)–C(31)	89.8 (1)
C(25)–Cr(1)–C(31)	178.3 (1)	Li(1)–Cr(1)–Li(2)	110.2 (2)
Li(1)–Cr(1)–Li(3)	110.2 (2)	Li(2)–Cr(1)–Li(3)	110.1 (2)

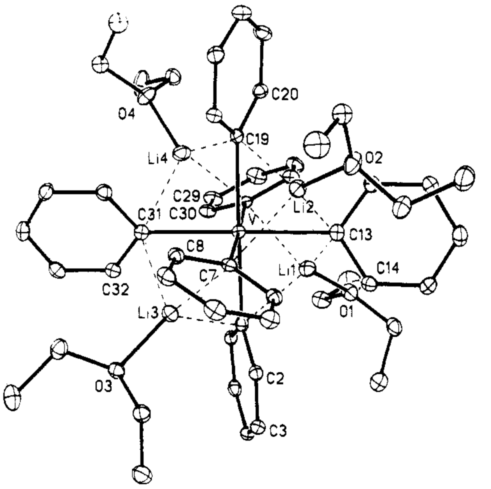

Figure 1. Thermal ellipsoid (30% probability) plot of 1. H atoms omitted for clarity.

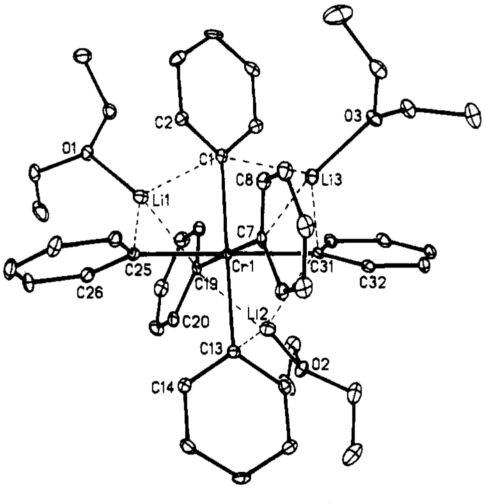

Figure 2. Thermal ellipsoid (30% probability) plot of one of the crystallographically independent molecules of 2. H atoms omitted for clarity.

This, together with differences in dihedral angles between the two complexes, led us to affirm the space group as $P\bar{1}$ with two nearly identical complexes per asymmetric unit. Further details are in Table I. An absorption correction was applied,[19] and structural refinement proceeded smoothly in both cases although disorded ethyl groups are present in two of the ethers in 1. All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were refined by using a riding model in which an idealized C–H vector of 0.96-Å length was recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. Final blocked-cascade least-squares refinement (based on F) converged at $R = 0.036$ and $R_W = 0.039$ using 4164 reflections with $I > 2\sigma(I)$ for 1 and $R = 0.049$ and $R_W = 0.054$ using 10491 reflections with $I > 3\sigma(I)$ for 2. Atom

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(19) Program XABS was written by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences.

coordinates for 1 and 2 are provided in Table II. Selected bond distances and angles are in Table III. Computer-generated thermal ellipsoidal plots of 1 and 2 are given in Figures 1 and 2.

Structural Description

[(LiEt$_2$O)$_4$VPh$_6$] (1). Compound 1 exists as discrete [(LiEt$_2$O)$_4$VPh$_6$] formula units. The vanadium(II) center is surrounded by six η^1-phenyl groups giving a VC$_6$ configuration which is very close to octahedral. The possibility of T_h symmetry for the VPh$_6$ system is precluded by significant dihedral angles between the phenyl groups and the three σ_h planes. For example the trans pairs of Ph rings C(1), C(19) and C(7), C(25) have dihedral angles of 20.9° and 67° with respect to the C(1), C(7), C(19), C(25) plane. The average V–C distance is near 2.35 Å, and the C–C distances of the phenyl rings are within normal ranges. The structure is completed by four lithium ions which cap alternate C$_3$ faces of the octahedron, 1.26 Å above each face. Thus, the four Li$^+$ ions themselves form a fairly regular tetrahedron with vanadium at its center and the phenyl groups bridge each of the six Li–Li edges which average 4.28 Å in length. Each Li$^+$ ion is also solvated by one ether molecule at an average Li–O distance of 1.933 Å, giving a pseudotetrahedral (three carbons and one oxygen) environment for each Li$^+$. The Li–C distances average 2.285 Å, and there are no other short Li–C contacts. The V···Li vectors average 2.615 Å in length.

[(LiEt$_2$O)$_3$CrPh$_6$] (2). The chromium complex 2 is in many respects similar to 1. There are two chemically and structurally similar, but crystallographically independent, [(LiEt$_2$O)$_3$CrPh$_6$] complexes in the unit cell. Broadly speaking, the structures are the same as 1 except that one of the four ions bridging alternate octahedral C$_3$ faces has been removed. Thus, the remaining three Li$^+$ ions together with Cr are in an arrangement of C_{3v} symmetry, each Li$^+$ ion being approximately 1.25 Å above the C$_3$ face. The CrC$_6$ moiety is close to octahedral, but only slight deviations from ideal geometry in the angles at Cr are apparent. This is somewhat surprising in view of its asymmetric nature. The average length for the Cr–C bonds is 2.25 Å, and the Li–C distances average 2.29 Å. The Li–O bonds are all near 1.91 Å, and the Li···Cr vectors are approximately 2.66 Å.

Discussion

The syntheses of compounds 1 and 2 were relatively straightforward and gave moderate yields of well-formed crystals of the products. The synthesis of the vanadium complex had not been previously described in detail. It was first mentioned in a note in 1960[7] and formulated as [(LiPh$_4$)VPh$_2$·3.5Et$_2$O]. There is some confusion surrounding the chromium species. This complex was first described in 1958 and formulated as [(LiPh)$_3$CrPh$_3$·2.5Et$_2$O].[15] It was synthesized from CrCl$_3$, and our results are in close agreement with this formulation. The same complex, however, can be obtained starting with CrCl$_2$ so that some oxidation of Cr(II) to Cr(III) has occurred. This result seems to be inconsistent with the report that the Cr(II) complex Li$_2$CrPh$_4$·4THF could be obtained as yellow crystals from CrCl$_2$(THF)$_2$/LiPh mixtures.[11] However, analytical and magnetic data support a high-spin d^4 formulation of the Li$_2$CrPh$_4$·4THF complex.[11] There are also reports describing related complexes such as the blue-green Li$_2$[CrPh$_5$]·Et$_2$O[20] and the red Li[CrPh$_4$]·4DME. An X-ray structure of the sodium salt of the former has been reported,[21] but the structure of the latter is still unknown. Clearly, further work will be required to obtain a fuller picture of the structures possible in the CrCl$_3$ or CrCl$_2$/LiPh systems.

The structure of the vanadium complex 1 has much less precedent than the chromium species. Well-characterized vanadium(II) σ-bonded aryls are limited to dinuclear species with bidentate ligands. For example, the structure of [V$_2$(dmop)$_4$] [dmop = 2,6-dimethoxyphenyl) is dimeric with a possible V≡V triple bond and bridged by two tridentate and two bidentate dmop ligands.[22] A complex of formula Li$_2$V(dmop)$_4$ has also been prepared,[23] but its structure is unknown. The [(LiEt$_2$O)$_4$VPh$_6$] structure is a highly symmetric one with the coordination sphere of vanadium involving an interlocking C$_6$ octahedron and an Li$_4$ tetrahedron. The vanadium is formally V(II), affording a d^3 electron configuration which favors an octahedral symmetry for maximum ligand field stabilization. Magnetic and spectral data support this view. The ground-state electron configuration is d^3 or ^{4}F, and the UV visible spectrum reveals a broad absorption centered at 528 nm (18 940 cm^{-1}) with weak features being apparent at ~460 nm (21 740 cm^{-1}) and ~590 nm (16 950 cm^{-1}). The magnetic moment, $\mu_{\text{eff}} = 3.85\ \mu_B$, consistent with the presence of three unpaired electrons, has already been reported.[7]

Several details of the structure are noteworthy. The most obvious is the extreme length of the V–C bonds which average 2.352 (3) Å. These are far longer than the bridging VC bonds (2.206 (8) Å) seen in [V$_2$(dmop)$_4$].[22] Several factors contribute to the lengthening of the bonds, and these include the following: (i) higher coordination number of the vanadium, (ii) a high formal negative charge and low metal oxidation state on the VPh$_6^{4-}$ moiety, and (iii) all the phenyl groups are also involved in bridging to Li atoms. The last point is underlined by the fact that the Li–C distances are about 2.295 (6) Å long. This is slightly shorter than the average Li–C distance of 2.311 (5) Å in (PhLiEt$_2$O)$_4$.[24] On this basis a case could be made for considering the structure of 1 as a somewhat modified phenyllithium structure in which the phenyl groups sit above the edges rather than the faces of an Li$_4$ tetrahedron. This gives an Li$_4$Ph$_6$(Et$_2$O)$_4$ moiety made electrically neutral by a centrally located V(II). The shorter Li–C distances in 1 relative to (PhLiEt$_2$O)$_4$ are then justified on the basis that the phenyl groups are doubly bridging two Li$^+$ atoms in 1 whereas in (PhLiEt$_2$O)$_4$ they behave as triply bridging moieties. None of the Li–O distances are remarkable and are fully consistent with approximate tetrahedral coordination for Li$^+$. The Li···V vector is also fairly short and is within the sum (2.74 Å) of the covalent radii for Li and V. Li–V bonding could not be confirmed by Li^7 NMR due to paramagnetic signal broadening. It may be that such bonding is weak or nonexistent and the close approach of Li and V is imposed by the bridge bonds between metals and ligands.

In the case of the chromium compound, 2, there is, in addition to the comparisons which can be drawn with 1, data available on three related compounds: Na$_2$CrPh$_5$·3Et$_2$O·THF (3),[21] *fac*-CrPh$_3$(THF)$_3$ (4)[25] and Li$_3$CrMe$_6$·6-(0.5dioxane) (5).[26] In 3, Cr(III) is in a distorted trigonal-bipyramidal configuration with two solvated Na$^+$ ions

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being associated with the $CrPh_5^{2-}$ moiety. In this compound the Cr–C distances average 2.09 Å whereas in 4 they average an even shorter 2.06 Å. These bonds are a good deal shorter than those seen in 2 whose Cr–C distances average 2.24 Å. Similar arguments to those employed for the vanadium complex can be invoked to account for the long bonds. Obviously, the higher coordination in 2 compared to that in 3 and the greater negative charge of the $CrPh_6^{3-}$ moiety compared to those of 3 and the neutral 4 are factors in the lengthening of the bonds. In addition, all the Cr–C bonds in 2 are bridging whereas in 4 all the bonds are terminal. In comparison to the vanadium complex 1, the Cr–C bonds in 2 are shorter because of the higher metal oxidation state and that Cr, being farther to the right in the periodic table, is smaller than V. The octahedral coordination is again favored by the d^3 electron configuration. The Li–C bonds are very similar to those seen in 1. Another interesting feature of 2 is the asymmetric disposition of the Li^+ ions relative to the $CrPh_6^{3-}$ moiety. A more symmetric distribution could have been achieved if the Li bridged edges of the C_6 octahedron. Indeed, this is the case in the complex $Li_3CrMe_6{\cdot}6$-(0.5dioxane) (5) whose Cr–C distances are also exceedingly long at 2.3 Å as are the Cr–Li vectors at 2.7 Å. It could be argued that since CH_3^- is expected to be a better σ-donor than Ph^-, there is greater negative charge buildup in 5 and longer Cr–C bonds. In that case shorter Cr–Li contacts than those seen in 2 would be expected. However, longer distances, 2.7 vs 2.66 Å, are observed. This is probably a result of the different coordination spheres surrounding the Li^+ ions in the complexes. In 5, each Li^+ is coordinated to two strongly coordinating dioxanes, and as a result, the Li^+ ions are disposed to interact with two rather than three carbons. This results in the Li^+ ions bridging C_6 octahedron edges in 5 rather than their faces which is what is observed in 2.

In summary our results show that it is possible to fairly readily crystallize polyphenylated/Li^+ salts of some early transition metals. Presumably, similar crystallographic studies can be carried out on species of the group 4 transition metals as well as heavier members of group 6. Studies on these and related species are continuing.

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Registry No. 1, 113858-41-6; 2, 113858-42-7; VCl_3, 7718-98-1; $CrCl_2$, 10049-05-5; PhLi, 591-51-5.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (18 pages); listings of structural factors (87 pages). Ordering information is given on any current masthead page.

How Do μ_2-Bridging Ligands Affect Metal–Metal Bonds in a Triosmium or Triruthenium Framework

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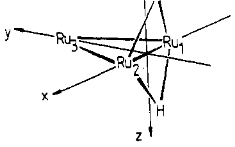
Fenske–Hall quantum chemical calculations have been performed on model complexes of general formula $HRu_3(CO)_{10}X$ (X = Cl, SH, and PH_2) in order to investigate the pattern in bonding of the μ_2-bridging groups to the metal framework in compounds $HM_3(CO)_{10}X$ (M = Ru and X = PHPh or SEt; M = Os and X = H, Cl, PHPh, SEt, $SCHPh_2$, or SC(H)=N-*p*-C_6H_4-F). It is shown that in the model compound $HRu_3(CO)_{10}SH$, the strengthening effect of the μ-SH group on the bridged metal–metal bond outweighs the weakening caused by the μ-H atom. The metal to main-group atom bridge bonding, rather than the direct metal–metal overlap, is responsible for the observed shortening of the bridged metal–metal bond, but the gross changes in metal–metal bonding caused by the bridging groups within the M(μ-H)(μ-X)M system are finely tuned by direct metal–metal overlap. Periodic trends as the group X varies in the model compound $HRu_3(CO)_{10}X$ are discussed. Along the series where X = PH_2, SH, or Cl, we show that the observed trend in bridged metal–metal bond lengths may be primarily attributed to a weakening of the interaction between the trimetal framework and the tangential orbital which is common to all three bridging groups. Changes in hybridization at the bridgehead atom, caused by the decreasing number of attached hydrogen atoms along the series, result in further perturbation of the trimetal to main-group interfragment bonding.

There is now characterized a wide variety of metal complexes of the general formula $HM_3(CO)_{10}X$ (M = Ru or Os), where X (X is group containing a second-row, group 15, 16, or 17 atom) and H are μ_2-ligands bridging the same metal–metal bond.[1-6] Other related complexes with first-row bridge groups have also been characterized.[7-15] It is well-known from the work of, for example, Churchill

Chart I



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