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Thermally Stable Allyl Zirconium Halide Compounds. Synthesis, Crystal Structure, and Dynamics of $(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}1,2,3\text{-}Me_3allyl)ZrBr_2$ and $(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}1,1,2\text{-}Me_3allyl)ZrBr_2$

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The reaction of Cp^*ZrCl_3 with $(1,1,2\text{-}Me_3allyl)MgBr$ or $(1,2,3\text{-}Me_3allyl)MgBr$ (previously unreported) and excess $MgBr_2$ yields $Cp^*(1,2,3\text{-}Me_3allyl)ZrBr_2$ and $Cp^*(1,1,2\text{-}Me_3allyl)ZrBr_2$, the first examples of thermally stable early-transition-metal compounds possessing both allyl and halide ligands. X-ray crystallography of these compounds shows a bent-metallocene-type geometry, with steric congestion in the asymetrically methylated compound causing significant distortion of the η^3-bound allyl ligand toward an η^1-binding mode. For $Cp^*(1,2,3\text{-}Me_3allyl)ZrBr_2$: cell constants $a = 14.615$ (6) Å, $b = 8.260$ (2) Å, $c = 14.669$ (5) Å; space group *Pbnm*; $R = 0.074$, $R_w = 0.076$. For $Cp^*(1,1,2\text{-}Me_3allyl)ZrBr_2$: cell constants $a = 9.197$ (2) Å, $b = 13.143$ (2) Å, $c = 14.586$ (3) Å, $\beta = 101.17$ (1)°; space group $P2_1/n$; $R = 0.056$, $R_w = 0.055$. A variable-temperature ^1H NMR study indicates that the allyl ligand in $(1,1,2\text{-}Me_3allyl)ZrBr_2$ undergoes η^3–η^1 isomerization [$\Delta G^{\ddagger}(-2\ °C) = 51.5 \pm 1.0$ kJ/mol].

Introduction

The η^5-Cp (C_5H_5) and η^5-Cp* (C_5Me_5) ligands, being effective electron donors, aromatic, and nonlabile, impart thermal stability to early-transition-metal compounds and are ubiquitous to early-transition-metal organometallic chemistry. In contrast, far fewer thermally stable allyl (C_3H_5) complexes of early transition metals are known. The allyl ligand is only a formal four-electron donor, it is smaller than Cp, and it often exhibits dynamic behavior such as η^3–η^1 isomerization.[1,2] Relative to Cp, the allyl ligand gives rise to a more accessible and electron-deficient metal center. We have set out to investigate allyl methylation as a means of enhancing the thermal stability of early-transition-metal allyl complexes. That methylation of organic ligands leads to increased donor ability,[3] and increased thermal stability of their metal complexes[4] has been well established for other cases. However, few reports exist in the literature for early-transition-metal comlexes of allyl ligands $[C_3H_{5-n}(Me)_n]$ with $n > 2$,[5] and the allylating reagents necessary for their preparation (Grignards or lithium compounds) are almost totally unknown. Also unknown are thermally stable early-transition-metal compounds possessing both halide and allyl ligands. For example, $Cp(allyl)ZrCl_2$ has been reported to decompose in solution above −40 °C.[6] Such compounds would serve two purposes: (1) They would allow for probing the extent of allyl methylation necessary to achieve high thermal stability, and (2) they would permit for further functionalization at the zirconium–halide bonds (attachment of R, PR_2, another metal, etc.) to yield other Cp*–allyl early-transition-metal complexes.

We report here on the highest yield syntheses yet of the two trimethylallyl Grignard reagents $(1,2,3\text{-}Me_3allyl)MgBr$ (**3**) and $(1,1,2\text{-}Me_3allyl)MgBr$ (**4**) (**3** has not been reported previously). We also report on the preparation, X-ray structural characterization, and dynamic behavior of $Cp^*(1,2,3\text{-}Me_3allyl)ZrBr_2$ (**5**), and $Cp^*(1,1,2\text{-}Me_3allyl)ZrBr_2$ (**6**), the first examples of thermally stable early-transition-metal complexes possessing both allyl and halide ligands.

Experimental Section

General Comments. The bromo allyls [1,2,3-trimethylallyl bromide (**1**) and 1,1,2-trimethylallyl bromide (**2**)] were prepared as described elsewhere.[7] Ether, tetrahydrofuran, and hexane were distilled from sodium/benzophenone under argon. The allyl Grignard solutions were titrated for organomagnesium species via the method of Eastham and Watson[8] and for total base content using HCl/NaOH (the Grignard yields reported below quote the results of the first method). Zirconium tetrachloride and 50-mesh Mg were purchased from the Aldrich Chemical Co. and used without further purification. All syntheses and subsequent handling of compounds were conducted under anhydrous conditions in a dry argon atomosphere.

$(1,2,3\text{-}Me_3allyl)MgBr$ (3). Magnesium (50 mesh) (15.0 g, 617 mmol) was placed in a three-necked flask equipped with a stir bar, gas inlet, septum, and an addition funnel. Tetrahydrofuran (250 mL) was added, vigorous stirring was begun (continued throughout the entire reaction), and the flask was cooled with an ice bath. Dibromoethane (5.0 mL, 58.0 mmol) was syringed in to activate the magnesium, followed after 30 min by addition of 1,2,3-trimethylallyl bromide (**1**) (3.18 g, 19.5 mmol) in THF (100 mL) over a 3-h period. The solution was stirred for an additional 2 h while allowed to warm to room temperature (yield 0.0386 M, 69%) [yields determined via HCl/NaOH titration were consistently 4–5% higher than yields determined by the method of Eastham and Watson[8] for both compounds **3** and **4**]. GC/MS investigation of an aliquot of Grignard solution quenched first with excess acetaldehyde and then with excess water showed three

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[1] (a) Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211. (b) Tsutusi, M.; Courtney, A. *Ibid.* **1977**, *16*, 241.

[2] Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642.

[3] Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

[4] Bonnemann, H.; Grard, C.; Kopp, W.; Pump, W.; Tanaka, K.; Wilke, G. *Angew. Chem.* **1973**, *12*, 964.

[5] (a) Faller, J. W.; Whitmore, B. C. *Organometallics* **1986**, *5*, 752. (b) de Liefde Meijer, H. J.; Jellinek, F. *Inorg. Chim. Acta* **1970**, *4*, 651. (c) Hendrik, M.; Jellinek, F. *J. Organomet. Chem.* **1968**, *12*, 149.

[6] Erker, G.; Berg, K.; Kruger, C.; Muller, G.; Angermund, K.; Benn, R.; Scroth, G. *Angew. Chem.* **1984**, *23*, 455.

[7] Van Zyl, C. M.; McKeeby, J. L.; Van Dort, P. C.; Larson, E. J.; Silver, M. E.; Huffman, J. C., accepted for publication in *Inorg. Chim. Acta.*

[8] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

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isomers of coupled bis(allyl) [mass spectrum, *m/e* (relative intensity) 166 (M^+, 5.2), 83 (100), 166 (M^+, 10.2), 83 (100), 166 (M^+, 4.4), 83 (100)] and two isomers of the expected 3,4-dimethyl-5-hydroxyhex-2-ene [mass spectrum, *m/e* (relative intensity) 128 (M^+, 3.6), 69 (100), 128 (M^+, 4.6), 69 (100)]. A second titration (Eastham and Watson) after 24 h at room temperature revealed no decrease in concentration, whereas a third titration after 1 week at room temperature displayed no organomagnesium species.

(1,1,2-Me$_3$allyl)MgBr (4). The method of preparation was similar to that used for compound **3** except that ether was used as the solvent [50-mesh magnesium (15.0 g, 617 mmol) in 250 mL of ether; 1,1,2-trimethylallyl bromide (**2**) (3.12 g, 19.1 mmol) in 150 mL of ether] (yield 0.0305 M, 64%). GC/MS investigation of an aliquot of Grignard solution quenched first with excess acetaldehyde and then with excess water showed three isomers of coupled bis(allyl) [mass spectrum, *m/e* (relative intensity) 166 (M^+, 2.6), 55 (100), 166 (M^+, 4.6), 55 (100), 166 (M^+, 16.3), 83 (100)] and the expected 2,3-dimethyl-5-hydroxyhex-2-ene [mass spectrum, *m/e* (relative intensity) 126 ($M^+ - 2$, 0.3), 69 (100)]. Solutions of this Grignard stored at room temperature were stable for at least 2 weeks.

Cp*(1,2,3-Me$_3$allyl)ZrBr$_2$ (5). To a solution of Cp*ZrCl$_3$ prepared in situ[9] (HCp*, 1.65 mL, 10.5 mmol; *n*-BuLi, 10.0 mmol; ZrCl$_4$, 2.45 g, 10.5 mmol; 150 mL of ether) was added a THF solution of **3** (0.0334 M, 300 mL, 10.0 mmol). The reaction solution quickly changed from pale yellow through orange to a final dark red color. The reaction solution was then reduced in volume to ~60 mL via trap to trap distillation, and 100 mL of hexane was added. The solution was reduced in volume again to ~60 mL, and an additional 100 mL of hexane was added. The reaction mixture was then filtered and the precipitate washed with 100 mL of hexane, yielding a dark red filtrate. Successive crystallizations at −12 °C yielded 1.59 g (33.8%) of orange-red crystals (mp 142–145 °C). Anal. Calcd for $C_{16}H_{26}ZrBr_2$: C, 40.94; H, 5.58. Found: C, 40.96; H, 5.66. ^{1}H NMR (CDCl$_3$/TMS 2%): δ 2.12 (CH$_3$, Cp*, 15 H), 2.02, 1.94, 1.75 (allyl, 11 H). IR (cm^{-1}, Nujol mull): 1224 m, 1024 s, 972 w, 842 s, 803 w, 774 w, 721 m, 680 m, 593 w, 582 m, 515 m, 470 m, 414 w, 378 s, 365 sh, 327 s. IR (cm^{-1}, halocarbon grease mull): 2986 m, 2957 m, 2920 s, 2866 m, 1490 w, 1450 m, 1430 m, 1385 s.

Cp*(1,1,2-Me$_3$allyl)ZrBr$_2$ (6). To a solution of Cp*ZrCl$_3$ prepared in situ[9] [HCp*, 1.44 mL, 9.18 mmol; *n*-BuLi, 9.18 mmol; ZrCl$_4$, 2.14 g, 9.18 mmol; 150 mL of ether] was added an ether solution of **4** [0.0212 M, 410 mL, 8.69 mmol]. The reaction solution quickly changed from pale yellow through orange to a final dark brown color. The reaction solution was then reduced in volume to ~60 mL via trap to trap distillation, and 100 mL of hexane was added. The solution was reduced in volume again to ~60 mL, and an additional 100 mL of hexane was added. The reaction mixture was then filtered and the precipitate washed with 50 mL of hexane/ether (3:2), yielding a dark brown filtrate. The filtrate was cooled to −12 °C, yielding an orange-brown precipitate. Recrystallization from ether at −12 °C yielded 1.04 g (24.2%) of orange crystals (mp 142–146 °C). Anal. Calcd for $C_{16}H_{26}ZrBr_2$: C, 40.94; H, 5.58. Found: C, 40.63; H, 5.45. ^{1}H NMR (CDCl$_3$/TMS 2%) δ 2.34 (CH$_3$, allyl, 3 H), 2.16 (CH$_3$, Cp*, 15 H), 1.90 (CH$_3$, allyl, 3 H), 1.57 (br) (CH$_2$, allyl, 2 H), 0.31 (CH$_3$, allyl, 3 H). ^{13}C NMR (CDCl$_3$/TMS 2%) δ 138.4 (C, allyl), 125.5 (C, Cp*), 121.2 (C, allyl), 71.27 (CH$_2$, allyl, t, $J[^{13}C-^1H] = 144.0$ Hz), 24.8 (CH$_3$, allyl, qt, $J[^{13}C-^1H] = 127.7, 5.6$ Hz), 22.0 (CH$_3$, allyl, qq, $J[^{13}C-^1H] = 125.7, 4.8$ Hz), 21.6 (CH$_3$, allyl, qq, $J[^{13}C-^1H] = 127.1, 3.9$ Hz), 13.2 (CH$_3$, Cp*, q, $J[^{13}C-^1H] = 3.8$ Hz). IR (cm^{-1}, Nujol mull): 1571 w, 1292 w, 1260 w, 1187 w, 1161 sh, 1100 w, 1068 w, 1057 w, 1021 s, 970 w, 959 w, 891 m, 846 s, 804 m, 681 w, 641 w, 608 m, 594 w, 576 m, 511 m, 453 s, 420 s, 411 sh, 362 vs. IR (cm^{-1}, halocarbon grease): 2956 m, 2907 m, 2875 m, 1571 w, 1485 m, 1453 w, 1425 m, 1401 w, 1383 m, 1375 s.

Nuclear Magnetic Resonance Spectra. Proton chemical shifts were measured at ambient probe temperature (22.0 °C) with a Varian FT-80A 80-MHz spectrometer. ^{13}C NMR (^{1}H-decoupled and gated-decoupled), and variable-temperature (+60 to −72 °C) ^{1}H NMR spectra for **6** were measured with a Varian XL-300 300-MHz spectrometer. All samples were prepared as CDCl$_3$ solutions: peak positions are reported as δ in parts per million downfield relative to TMS at δ 0. Temperatures, determined by using a methanol standard, are estimated to be accurate to ±0.5 °C.

Table I. Summary of Crystal Data and Intensity Collection for Cp*(1,2,3-Me$_3$allyl)ZrBr$_2$ (5) and Cp*(1,1,2-Me$_3$allyl)ZrBr$_2$ (6)

	5	**6**
formula	$C_{16}H_{26}ZrBr_2$	$C_{16}H_{26}ZrBr_2$
fw	469.41	469.41
a, Å	14.615 (6)	9.197 (2)
b, Å	8.260 (2)	13.143 (2)
c, Å	14.669 (5)	14.586 (3)
β, deg		101.17 (1)
V, Å^3	1771.00	1727.27
Z	4	4
d, g cm^{-3}	1.761	1.803
space group	*Pbnm*	$P2_1/n$
cryst dimens, mm	{001}, *d* = 0.0450; {001}, *d* = 0.0450; {100}, *d* = 0.0400; {110}, *d* = 0.0400; {321}, *d* = 0.0400	0.13 × 0.24 × 0.25
transmissn factors[a]	0.6470–0.7150	
temp, °C	−155 °C	−155 °C
radiatn	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
linear abs coeff, cm^{-1}	50.691	51.901
receiving aperture	3.0 × 4.0 mm; 22.5 cm for xtal	3.0 × 4.0 mm; 22.5 cm from xtal
takeoff angle, deg	2.0	2.0
scan speed	4° in 2θ/min	4° in 2θ/min
scan width	2° + dispersion	2° + dispersion
bkgd counts	6 s at each end	6 s at each end
2θ limits, deg	6–45	6–45
data collected	$+h,+k,+l$	$+h,+k,\pm l$
unique data	2688	2263
unique data with $F_o^2 > 2.33\sigma(F_o^2)$ for **5** and $F_o^2 > 3\sigma(F_o^2)$ for **6**	1453	1943
R(*F*)	0.0736	0.0562
$R_w(F)$	0.0759	0.0554

[a] *s* The analytical method, as employed in the absorption program AGNOST, was used for the absorption correction (de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018).

Infrared Spectra. Infrared spectra were measured in the region 4000–300 cm^{-1} with a Nicolet 20-DX spectrophotometer equipped with a CsI beam splitter. The compounds were studied as mineral oil mulls and as Halocarbon 25-5S grease mulls (polychlorotrifluoroethylene oils thickened with silica gel, Halocarbon Products Corp., NJ, have no absorptions between 1300 and 4000 cm^{-1}) between CsI plates. The estimated uncertainty in reported frequencies is ±2 cm^{-1}.

Mass Spectra. Mass spectra were measured on a Hewlett-Packard 5995A mass spectrometer (EI at 70 eV) with the use of a GC inlet system.

Melting Points. Melting points were measured in sealed, evacuated capillaries by using a calibrated thermometer.

X-ray Structural Determination. Pertinent data for the structures of compounds **5** and **6** are in Table I. The crystals were mounted on a Picker computer-controlled four-circle diffractometer equipped with a Furnas Monochromator (HOG crystal) and cooled by a gaseous nitrogen cooling system. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with systematic absences and symmetry consistent with the orthorhombic space group *Pbnm* for **5** and the monoclinic space group $P2_1/n$ for **6**. Orientation matricies and accurate unit cell dimensions were determined at low temperature from least-squares fits of 32 reflections (20° < 2θ < 30°) for both **5** and **6**. Intensity data were collected by using the $\theta/2\theta$ scan method; four standard reflections, monitored every 300 reflection measurements, showed only statistical fluctuations for both compounds. An absorption correction was performed on compound **5** (see Table I). An absorption correction for **6** was

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(9) Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319.

Table II. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors for 5 and 6[a]

		5					**6**		
atom	x	y	z	B(eq), Å^2	atom	x	y	z	B(eq), Å^2
Zr	5236 (1)	3570 (2)	7500*	0.6	Zr	5914 (1)	2521 (1)	3591 (1)	1.1
Br	5504 (1)	5600 (2)	8772 (1)	2.8	Br(1)	7856 (1)	1035 (1)	3887 (1)	2.1
Br′	5504 (1)	5600 (2)	6228 (1)	2.8	Br(2)	5933 (1)	2846 (1)	5322 (1)	2.5
C(1)	6323 (7)	1832 (13)	8320 (9)	1.4	C(1)	4245 (12)	880 (9)	3179 (7)	2.1
C(1)′	6323 (7)	1832 (13)	6680 (9)	1.4	C(2)	3419 (12)	1622 (9)	3515 (7)	1.9
C(2)	6766 (10)	2181 (18)	7500*	1.3	C(3)	3365 (12)	2637 (10)	3129 (9)	1.9
C(3)	6718 (9)	2158 (16)	5733 (9)	1.9	C(4)	4442 (18)	−179 (11)	3548 (13)	3.2
C(3)′	6718 (9)	2158 (16)	9267 (9)	1.9	C(5)	2694 (14)	1460 (11)	4365 (8)	2.3
C(4)	7592 (12)	3221 (20)	7500*	1.7	C(6)	4694 (14)	1059 (11)	2252 (8)	2.3
C(5)	4173 (10)	1090 (18)	7500*	1.2	C(7)	6111 (13)	3638 (8)	2230 (7)	1.9
C(6)	3978 (7)	2036 (14)	6711 (8)	1.0	C(8)	7548 (13)	3235 (8)	2569 (8)	2.0
C(6)′	3978 (7)	2036 (14)	8289 (8)	1.0	C(9)	8083 (12)	3656 (9)	3468 (8)	2.0
C(7)	3600 (7)	3511 (15)	7017 (8)	1.3	C(10)	6979 (11)	4315 (8)	3700 (6)	1.4
C(7)′	3600 (7)	3511 (15)	7983 (8)	1.3	C(11)	5772 (11)	4302 (8)	2948 (7)	1.4
C(8)	4470 (12)	−658 (24)	7500*	2.1	C(12)	5221 (19)	3536 (12)	1282 (9)	2.8
C(9)	4074 (8)	1553 (16)	5733 (9)	1.8	C(13)	8402 (19)	2575 (12)	2024 (12)	3.5
C(9)′	4074 (8)	1533 (16)	9267 (9)	1.8	C(14)	9581 (15)	3493 (13)	4074 (12)	3.0
C(10)	3192 (9)	4781 (16)	6399 (9)	2.2	C(15)	7168 (20)	5005 (11)	4523 (9)	2.5
C(10)′	3192 (9)	4781 (16)	8601 (9)	2.2	C(16)	4415 (18)	4937 (14)	2834 (13)	2.9

[a] Parameters marked by an asterisk (*) were not varied. Estimated standard deviations are given in parentheses. Equivalent isotropic temperature factors are calculated by using the formula given by; Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

not done since the irregular shape of the crystal prevented indexing of the faces. However, the structure was refined successfully without this correction. The intensities were corrected for Lorentz and polarization factors and scaled to give the numbers of independent F_{hkl} values for $I > 3\sigma(I)$ indicated in Table I.

Both structures were solved by a combination of direct methods (MULTAN78) and Fourier techniques. All atoms, including hydrogens, were located for both compounds. All non-hydrogen atoms for both compounds and the hydrogen atoms for **6** were refined. The hydrogen atoms for **5** did not refine well; their idealized positions (C–H = 0.95 Å) were used and not varied; they were assigned fixed isotropic thermal parameters by adding 1.0 Å^2 to the equivalent isotropic thermal parameter of the attached C atom. Full-matrix least-squares refinements included ansiotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms; refinements converged to values for the conventional R indicies shown in Table I. The maximum residual in the final difference Fourier synthesis for **5** was 0.95 e/Å^3. The final difference Fourier synthesis for **6** was essentially featureless, with the largest peak being 0.30 e/Å^3. The weighting scheme used in the final calculations was of the form $w = 1/\sigma_F^2$. Scattering factors for the atoms were taken from ref 10. The scattering factor for the Zr and Br atoms were corrected for the real and imaginary parts of anomalous dispersion by using values from ref 10. All computations were carried out on a CDC Cyber 170-855 computer using programs described elsewhere.[11] The positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table II, the atom-numbering schemes being shown in Figure 1 for compounds **5** and **6**. Anisotropic thermal parameters for the non-hydrogen atoms are listed in Table III (supplementary material), hydrogen atom coordinates and isotropic thermal parameters in Table IV (supplementary material), and structure factors in Tables V and VI (supplementary material) for compounds **5** and **6**, respectively.

Results and Discussion

Synthesis of Methylated Allyl Magnesium and Zirconium Compounds. Solutions of the trimethylallyl Grignards **3** (in THF) and **4** (in ether) also contained MgBr$_2$, formed from activating the Mg with dibromoethane and from competitive coupling to produce bis(allyls). The 1,1,2-trimethylallyl Grignard **4** has been prepared previously but at lower yield than reported here.[12] Ether solutions of **4** are stable at room temperature for long periods. The 1,2,3-trimethylallyl Grignard **3**, previously unreported, had to be prepared in THF due to its decomposition in ether (complete within 20 h at both room temperature and −78 °C). Even THF solutions of **3** were stable for only a few days and were thus used within 24 h of their preparation. While we did not attempt to isolate the decomposition products, reactivity similar to that of highly substituted organolithiums with ethereal solvents may be involved.[13] The zirconium allyl compounds **5** and **6** were prepared at room temperature by addition of a dilute ether or THF solution of the appropriate allyl Grignard to a stirred ether solution of Cp*ZrCl$_3$ prepared in situ.[9] The low reaction yields are not a consequence

$$\mathrm{Cp^*ZrCl_3} + \underset{\mathbf{3,\,4}}{\mathrm{(allyl)MgBr}} + \mathrm{xs\ MgBr_2} \rightarrow \underset{\mathbf{5,\,6}}{\mathrm{Cp^*(allyl)ZrBr_2}}$$

3, **5**, allyl = 1,2,3-trimethylallyl; **4**, **6**, allyl = 1,1,2-trimethylallyl

of thermal instability, as might be expected for lesser methylated analogues.[6,14] Both compounds **5** and **6** melt without decomposition above 140 °C, and CDCl$_3$ solutions in sealed NMR tubes show only minor degradation after 1 week at room temperature. Removal of solvent from the filtrates recovered after isolating crystals of **5** and **6** yield uncharacterized oils. Efforts to either increase yields or isolate other products are continuing, and the possibility that the Grignards are also reducing the metal is being explored.[5c,15]

The isolation of Cp*–(trimethylallyl) zirconium compounds **5** and **6** demonstrates that ligand methylation is an effective way to increase the thermal stability of formally electron-deficient early-transition-metal complexes. For example, the analogous unmethylated Cp(allyl)ZrCl$_2$ has been reported to decompose in solution above −40 °C,[6] and the monomethylallyl compounds Cp*M(1-Meallyl)$_3$ [M = Ti, Zr; at least one allyl is η^3-bound] convert to

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(10) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

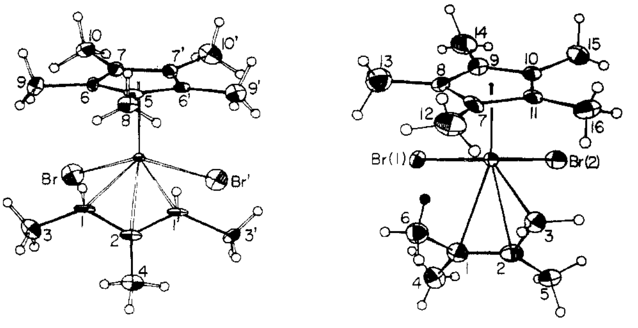
(11) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

(12) Lion, C.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1976**, 1876.

(13) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, 1974; p 198.

(14) (a) de Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383. (b) Berg, K.; Erker, G. *Ibid.* **1984**, *270*, C53. (c) Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.; Zimmermann, H. *Angew. Chem.* **1966**, *5*, 151.

(15) (a) Martin, H. A.; Jellinek, F. *J. Organomet. Chem.* **1967**, *8* 115. (b) Martin, H. A.; Lemaire, P. J.; Jellinek, F. *Ibid.* **1968**, *14*, 149.



5 6

Figure 1. ORTEP diagrams of Cp*(1,2,3-Me_3allyl)$ZrBr_2$ (5) and Cp*(1,1,2-Me_3allyl)$ZrBr_2$ (6). The darkened methyl hydrogen on C(6) for 5 is 2.34 (9) Å from the Zr atom.

allyl-butadiene metal complexes at or below −40 °C.[14a,b] The thermal stability of 5 and 6 is more like that of the closely related zirconocene dihalides. In contrast to the zirconocene dihalides, compounds 5 and 6 are very air-sensitive, decomposing within minutes upon exposure to the atmosphere.

Molecular Structures for 5 and 6. Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of 5 and 6 are presented in Table II; bond distances and angles for both compounds are given in Table VII. Perspective views showing the molecular geometry and the atom numbering schemes are presented in Figure 1. In the orthorhombic unit cell for 5 each molecule lies on a crystallographic mirror plane passing through atoms C(2), C(4), C(5), C(8), and Zr, whereas in the monoclinic cell for 6, each molecule occupies a general position. The molecular structures of 5 and 6 are similar to that of a bent metallocene, with the plane defined by the Zr and two Br atoms and the plane defined by the Zr atom and the allyl and Cp* centroids being orthogonal in 5 and nearly orthogonal (dihedral angle of 86.2 °) for 6. The Cp*(centroid)–Zr–allyl(centroid) angles are 118.4° and 134.8° for 5 and 6 respectively. Crystallographic studies have established that the corresponding Cp(centroid)–metal–Cp(centroid) angle in a bent metallocene can vary from 148° in Cp_2MoH_2 to 126° in Cp_2ZrI_2.[16] The larger angle in 6 (relative to 5) is likely due to crowding between allyl methyl C(6) and Cp* methyl C(12) [the nonbonded contact is 0.38 Å less than the sum of the van der Waals radii,[17,18] no such repulsive contacts exist in 5].

As observed elsewhere,[19] all of the Cp* methyl groups are bent out of the Cp* plane away from the Zr atom for 5 and 6, and the normal to the Cp* plane is essentially colinear with the Zr–Cp*(centroid) vector (angles of 3.0° and 1.6° for 5 and 6, respectively). The unique aspects of these structures involve the metal–allyl bonding and are best visualized by associating a square-pyramidal geometry with 5 and 6 such that the Cp* ligand assumes an apical position, the two Br atoms occupy two adjacent basal positions, and the allyl ligand occupies the remaining two basal positions. Typically, the central carbon atom of the allyl ligand points down, toward the basal plane.[6] While this is the case for the 1,2,3-trimethylallyl compound 5, the 1,1,2-trimethylallyl ligand in 6 is rotated about its Zr–centroid vector by 53.0° such that its unsubstituted end is rotated toward the apical Cp*. In addition, the allyl ligand planes of 5 and 6 are tilted, the angle between the normal to the allyl plane and the Zr–allyl(centroid) vector being 29.4° and 32.8°, respectively [this is similar to the tilt of 27.5° observed for (η-cyclooctatetraenyl)(η-allyl)(t-C_4H_9O)Zr].[20] The tilt is such that the central allyl carbon atom moves away from the Zr atom while the terminal allyl carbons move closer. This results in a longer Zr–C distance to the central allyl carbon atom [2.513 (14) Å] than to the terminal allyl carbon atoms [2.456 (11) Å] for the 1,2,3-trimethylallyl compound 5. The 1,1,2-trimethylallyl ligand in 6 displays the same tilt, with a longer Zr–C(2) distance to the central allyl carbon atom [2.565 (11) Å] than to the unsubstituted terminal allyl C(3) atom [2.316 (11) Å]. However, there is an elongation of the Zr–C bond to the dimethylated allyl carbon atom C(1) [2.648 (11) Å]. Both the elongated Zr–C(1) bond length and the rotation of the

Table VII. Bond Distances (Å) and Angles (deg) in 5 and 6

atoms	dist	atoms	angle
		5	
Zr–Br	2.538 (2)	Br–Zr–Br	94.6 (1)
Zr–C(1)	2.456 (11)	Ct(Cp)–Zr–Ct(al)[a]	118.4 (4)
Zr–C(2)	2.513 (15)	C(2)–C(1)–C(3)	124.8 (10)
Zr–C(5)	2.571 (15)	C(1)–C(2)–C(4)	119.8 (7)
Zr–C(6)	2.515 (11)	C(1)–C(2)–C(1)′	119.0 (12)
Zr–C(7)	2.495 (10)	C(6)–C(5)–C(6)′	108.9 (12)
Zr–Ct(al)[a]	2.247 (12)	C(6)–C(5)–C(8)	125.6 (7)
Zr–Ct(Cp)[a]	2.111 (12)	C(5)–C(6)–C(7)	107.1 (10)
C(1)–C(2)	1.396 (15)	C(5)–C(6)–C(9)	127.9 (11)
C(1)–C(3)	1.528 (18)	C(7)–C(6)–C(9)	124.9 (11)
C(2)–C(4)	1.482 (23)	C(6)–C(7)–C(7)′	108.5 (10)
C(5)–C(6)	1.425 (14)	C(6)–C(7)–C(10)	124.3 (11)
C(5)–C(8)	1.508 (25)	C(7)′–C(7)–C(10)	126.9 (11)
C(6)–C(7)	1.411 (17)		
C(6)–C(9)	1.496 (18)		
C(7)–C(7)′	1.417 (17)		
C(7)–C(10)	1.509 (18)		
		6	
Zr–Br(1)	2.625 (2)	Br(1)–Zr–Br(2)	95.04 (6)
Zr–Br(2)	2.557 (2)	Ct(Cp)–Zr–Ct(al)[a]	134.8 (4)
Zr–C(1)	2.648 (11)	C(2)–C(1)–C(6)	118.2 (10)
Zr–C(2)	2.565 (11)	C(2)–C(1)–C(4)	124.6 (12)
Zr–C(3)	2.316 (11)	C(4)–C(1)–C(6)	115.7 (12)
Zr–C(7)	2.504 (11)	C(1)–C(2)–C(3)	119.5 (11)
Zr–C(8)	2.496 (13)	C(1)–C(2)–C(5)	122.9 (11)
Zr–C(9)	2.525 (12)	C(3)–C(2)–C(5)	117.1 (11)
Zr–C(10)	2.547 (10)	C(8)–C(7)–C(11)	106.9 (8)
Zr–C(11)	2.516 (10)	C(8)–C(7)–C(12)	127.2 (12)
Zr–Ct(al)[a]	2.282 (11)	C(11)–C(7)–C(12)	125.3 (11)
Zr–Ct(Cp)[a]	2.208 (11)	C(7)–C(8)–C(9)	108.0 (10)
C(1)–C(2)	1.383 (17)	C(7)–C(8)–C(13)	125.4 (10)
C(1)–C(4)	1.490 (19)	C(9)–C(8)–C(13)	126.3 (11)
C(1)–C(6)	1.506 (17)	C(8)–C(9)–C(10)	108.7 (9)
C(2)–C(3)	1.445 (18)	C(8)–C(9)–C(14)	127.1 (12)
C(2)–C(5)	1.533 (17)	C(10)–C(9)–C(14)	124.2 (11)
C(7)–C(8)	1.420 (16)	C(9)–C(10)–C(11)	107.4 (9)
C(7)–C(11)	1.443 (15)	C(9)–C(10)–C(15)	125.8 (10)
C(7)–C(12)	1.470 (16)	C(11)–C(10)–C(15)	126.2 (11)
C(8)–C(9)	1.421 (16)	C(7)–C(11)–C(10)	109.0 (9)
C(8)–C(13)	1.498 (22)	C(7)–C(11)–C(16)	123.7 (10)
C(9)–C(10)	1.425 (16)	C(10)–C(11)–C(16)	127.0 (11)
C(9)–C(14)	1.501 (17)		
C(10)–C(11)	1.402 (12)		
C(10)–C(15)	1.488 (16)		
C(11)–C(16)	1.484 (20)		

[a] The centroid of the allyl and Cp ligands are presented as Ct(al) and Ct(Cp), respectively.

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(16) (a) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2290. (b) Guggenberger, L. J. *Inorg. Chem.* **1973**, *12*, 232. (c) Melmed, K. M.; Coucouvanis, D.; Lippard, S. J. *Ibid.* **1973**, *12*, 232.

(17) We take the van der Waals radius of a methyl group and a hydrogen atom to be 2.0 and 1.2 Å, respectively.[18] A lower limit of 1.45 Å, the covalent radius of Zr, is taken for the van der Waals radius of Zr, which is not known.

(18) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed; Cornell University: Ithaca, NY, 1960; p 260.

(19) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(20) Brauer, D. J.; Kruger, C. *Organometallics* **1982**, *1*, 204.

ligand about its centroid in 6 are due to the increased bulk at the dimethylated end of the 1,1,2-trimethylallyl ligand and the resulting methyl(Cp*)–methyl(allyl) repulsive contact mentioned previously. The result is that compound 6 has the widest range of Zr–C(allyl) bond lengths [2.316 (11)–2.648 (11) Å] yet observed for a Zr–allyl complex [the previous widest range was from 2.448 (5) to 2.517 (5) Å,[20] and the range is typically smaller[6,21]]. As a consequence, 6 may be thought of as possessing an η^3-allyl ligand that has been significantly distorted toward an η^1-binding mode in which the dimethylated end is no longer bound to the metal. This is further supported by the wide variation in the C–C bond lengths within the allyl ligand in 6 [C(1)–C(2) = 1.383 (17) Å; C(2)–C(3) = 1.445 (18) Å], significantly lengthening the C(2)–C(3) bond that would be a single bond in the η^1-form [the C–C bond length within the allyl ligand of 5 is 1.396 (15) Å]. The results of a variable-temperature ^{1}H NMR study indicating that the allyl ligand in 6 undergoes rapid η^3-η^1 isomerization via bond rupture only at the dimethylated end of the ligand (vide infra) are consistent with this X-ray result.

Another structural feature unique to 1,1,2-trimethylallyl compound 6 is the relatively short distance [2.34 (9) Å] between the Zr atom and the methyl hydrogen atom H(18) [shown in Figure 1 as the blackened hydrogen atom on the methyl group C(6)]. This distance is only 0.29 Å longer than the Zr–H(bridging) distance in $[(\eta^5\text{-}C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$[22] and is well within the sum of the van der Waals' radii of the Zr and H atoms.[17] Such a distance, along with the formal 14-electron count for 6, warrants consideration that this hydrogen atom is agostic in nature.[23] The Zr–H(18) distance in 6 is 0.14 Å less than the shortest Zr–H separation in Zr(dmpe)$[CH_2Si(CH_3)_3]_4$, where an agostic interaction is postulated on the basis of crystallographic and infrared results.[24] Both extended Hückel[25a] and CNDO/2[25b] calculations on 6 show a small but significant bond order between this hydrogen (and no other hydrogen) and the metal atom. However, the C(6)–H(18) bond length [0.96 (2) Å] and angles involving this hydrogen are not substantially different from any others in the structure, nor is there any evidence of a weakened C–H stretch [2700–2350 cm^{-1}] sometimes observed for agostic hydrogens[23,24b] [C–H stretching for 6 occurs from 2956 to 2875 cm^{-1}]. a small J_{C-H} in the ^{13}C NMR spectrum is a good diagnostic for an agostic interaction.[23] The allyl methyl region in the gated-decoupled ^{13}C NMR spectrum of 6 (see Experimental Section) displays no such reduced coupling constant. This region exhibits three separate quartets with nearly identical J_{C-H} values of 127.7, 125.7, and 127.1 Hz [these quartets were further resolved into triplets (J_{C-H} = 5.6 Hz), quartets (J_{C-H} = 4.8 Hz), and quartets (J_{C-H} = 3.9 Hz), respectively, consistent with second-order C–H coupling through three bonds]. We therefore conclude that the H(18) atom in 6 is not agostic, and the relatively short Zr–H(18) distance is a consequence of the steric crowding mentioned previously. The fact that both 5 and 6 have high thermal stability demonstrates that it is primarily the extent of ligand methylation and subsequent donor ability that is most important with respect to stabilizing these compounds. The structural differences between 5 and 6 are due to the different steric requirements of the symmetrically vs. the asymmetrically substituted trimethylallyl ligands.

Infrared spectroscopy has often been used to assign an η^1- or an η^3-bound configuration to allyl ligands in metal complexes [1650–1580 cm^{-1} for η^1-bound allyl, 1550–1450 cm^{-1} for η^3-bound allyl].[5b,26] Compounds 5 and 6 display absorptions at 1485 and 1490 cm^{-1}, respectively, indicative of η^3-binding. However, compound 6 shows an additional absorption at 1571 cm^{-1}. This is consistent with the X-ray observation that the η^3-bound 1,1,2-trimethylallyl ligand in 6 is significantly distorted toward an η^1-bound configuration.

Dynamic Behavior of 6. The ^{1}H NMR spectrum of 6 consists of five singlets (see Experimental Section). The occurrence of an allyl methyl resonance at δ 0.31, far upfield of the other methyl peaks, is unique to 6 [all methyl resonances for 5 occur between δ 2.17 and δ 1.75]. This leads us to tentatively assign the upfield methyl resonance in 6 to the unique methyl group C(6). The spectrum of 6 is consistent with the observed static structure found in the crystalline state with the exception that the terminal allylic CH_2 group should appear as an AX doublet of doublets. The inferred conclusion, that the 1,1,2-trimethylallyl ligand exhibits dynamic behavior, was confirmed by variable-temperature ^{1}H-NMR spectroscopy. Spectra were measured from −72 °C [CH_2, allyl, AX doublet of doublets at δ 2.04, 2.01 and δ 1.04, 1.01] to +60 °C [CH_2, allyl, sharpened singlet at δ 1.61], yielding a $\Delta G^{\ddagger}(-2\ ^\circ C) = 51.5 \pm 1.0$ kJ/mol, as estimated from the coalescence of the methylene protons. A mechanism for 6, whereby the η^3-1,1,2-trimethylallyl ligand becomes η^1 via rupture of the Zr–C bonds to the substituted carbon atoms, followed by rotation about the remaining Zr–C bond and return to the η^3-bonding mode, is consistent with this. Such η^3-η^1 isomerization for allyl complexes is well-known.[1,2] For example, this mechanism accounts for the observed dynamic behavior in (η^3-allyl)(η^4-butadiene)CpZr [$\Delta G^{\ddagger}(105\ ^\circ C) = 79.9 \pm 1.2$ kJ/mol], where bond rupture at either end of the allyl ligand is equally likely.[6] The methyl peaks for 6 remain as singlets up to 60 °C, indicating that isomerization to an η^1-mode in which the dimethylated carbon atom remains bound to zirconium does not occur. The mirror plane in 5 precludes a similar NMR investigation of η^3–η^1 isomerization. However, a study of substituted allyl compounds of palladium demonstrates that this isomerization is still possible even when the bound allyl carbon in the η^1-form is mono- or dimethylated [$\Delta G^{\ddagger}$ for the formation of an η^1-bonded intermediate increases from 70.1 to 87.4 to 99.2 kJ/mol when the bound carbon atom goes from unsubstituted to monomethylated to dimethylated, respectively].[2] This suggests that the 1,2,3-trimethylallyl ligand in 5 can undergo similar dynamic behavior in solution but would do so with a higher $\Delta G^{\ddagger}$ than that for 6.

Conclusions

Ligand methylation is an effective method for providing thermally stable early-transition-metal allyl complexes. It has, for the first time, allowed for the isolation of Cp*–allyl analogues of metallocene dihalides. However, they differ from metallocene dihalides in that they possess a ligand (trimethylallyl) which exhibits dynamic (η^3–η^1) behavior.

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(21) Highcock, W. J.; Mills, R. M.; Spencer, J. L; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 829 and references cited therein.

(22) Jones, S. B.; Peterson, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

(23) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(24) (a) Cayias, J. Z.; Babaian, E. A.; Hrncir, D. C.; Bott, S. G.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1986**, 2743. (b) Girolami, G. S.; Wilkinson, M.; Thornton-Pett, M.; Hursthouse, M. B. *Ibid.* **1984**, 2789.

(25) (a) Extended Hückel zirconium parameters are taken from: Hofmann, P.; Stauffert, P.; Patsuni, K.; Nakamura, A.; Hoffmann, R. *Organometallics* **1985**, *4*, 404. (b) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589. The CNDO/2 calculation was done on the analogous titanium compound.

(26) Hendrik, M. A.; Lemaire, P. J.; Jellinek, F. J. *J. Organomet. Chem.* **1968**, *14*, 149.

The thermal stabilities of these compounds are dependent on the extent of ligand methylation, while structural dissimilarities are due to the steric requirements dictated by the particular substitution pattern. Work is proceeding to further examine the effect of methylation on thermal stability and to investigate the potential of these Cp*–allyl dihalide compounds as starting points for the synthesis of other Cp*–allyl complexes via halide substitution.

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Registry No. 1, 109929-22-8; 2, 109929-23-9; 3, 109929-24-0; 4, 109929-25-1; 5, 109959-72-0; 6, 109959-71-9; Cp*ZrCl$_3$, 75181-07-6.

Supplementary Material Available: Tables of thermal parameters and hydrogen atom coordinates (3 pages); listings observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Electrochemical, Structural, and Spectroelectrochemical Investigations of (OEP)Ir(CO)Cl and (TPP)Ir(CO)Cl in Nonbonding Media

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The electrochemical and spectroelectrochemical properties of (P)Ir(CO)Cl, where P is the dianion of octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP), are reported. These compounds can be reversibly oxidized by up to two one-electron transfer steps that occur at the porphyrin macrocycle. A two-electron reduction of (OEP)Ir(CO)Cl with ultimate formation of [(OEP)Ir]$^-$ is observed at room temperature. Low-temperature studies indicate that this reduction initially occurs at the porphyrin π ring system and that the anion radical intermediate can be stabilized. A self-consistent oxidation and reduction mechanism is presented. The molecular structure of (OEP)Ir(CO)Cl was found to crystallize in the $P2_1/c$ space group with a = 8.52 Å, b = 13.09 Å, c = 20.04 Å, β = 92.40°, and Z = 2.0.

Introduction

Synthesis of the iridium porphyrin (P)Ir(CO)Cl where P = a porphyrin dianion was first reported in 1968,[1] but it was not until 10 years later that the chemical reactivity of this compound was characterized in any detail.[2] (OEP)Ir(CO)Cl[3] can be converted to (OEP)Ir(CH$_3$) by reaction with CH$_3$Li in THF. It may also be converted to (OEP)IrH and [(OEP)Ir]$^-$ by reduction with NaBH$_4$ in alkaline ethanol.[2] The hydride is the initial product in the synthesis of dimeric [(P)Ir]$_2$[4] while [(P)Ir]$^-$ can be converted to (P)Ir(R) by reaction with RX.[2]

Both dimeric [(P)Ir]$_2$ and the related σ-bonded (P)Ir(R) complexes have been the object of recent investigations.[4-6] It is known that (OEP)Ir(CO)Cl can be chemically reduced to give [(OEP)Ir]$^-$,[2,7] but a detailed electrochemical study of this reduction has never been presented. A structural characterization of (OEP)Ir(CO)Cl is also lacking in the literature.

(OEP)Ir(CO)Cl can be obtained as a product of the reaction involving (OEP)H$_2$ and either [Ir(CO)Cl]$_2$ or [Ir(COD)Cl]$_2$ where COD = 1,5-cyclooctadiene (eq 1).[2] In

$$\mathrm{(OEP)H_2 + [Ir(COD)Cl]_2 \rightarrow (OEP)Ir(C_8H_{13}) + (OEP)Ir(CO)Cl} \quad (1)$$

a recent publication we presented the structural and electrochemical properties of (OEP)Ir(C$_8$H$_{13}$).[8] This paper presents the structural and electrochemical properties of (OEP)Ir(CO)Cl and the related (TPP)Ir(CO)Cl. The structure of (OEP)Ir(CO)Cl is only the second iridium porphyrin structure that has ever been obtained.

Experimental Section

Materials. Dichloromethane was purified by double distillation from CaH$_2$. Tetrahydrofuran (THF) (HPLC grade) was purified by distillation from Na/benzophenone. Benzonitrile (PhCN) (reagent grade) was vacuum distilled over P$_2$O$_5$. Tetrabutylammonium perchlorate (TBAClO$_4$) and tetrabutylammonium chloride (TBACl) were recrystallized twice from absolute ethanol, dried, and stored under vacuum at 45 °C. High-purity nitrogen and carbon monoxide were purchased from IWECO and Matheson, respectively. (OEP)Ir(CO)Cl and (TPP)Ir(CO)Cl were synthesized according to literature procedures.[1,2] The purity of these compounds was checked by comparison with reported ^{1}H NMR, UV-visible and IR spectra.

Instrumentation. Cyclic voltammetric measurements were performed with an EG&G Model 173 potentiostat, an EG&G Model 175 Universal programmer, and a Houston Instruments Model 2000 X-Y recorder or a BAS 100 electrochemical analyzer. Controlled potential electrolysis was performed with an EG&G Model 173 potentiostat or a BAS 100 electrochemistry system. Rotating disk electrode (RDE) experiments were performed with an IBM EC 1219 rotating disk electrode controller coupled with one of the above listed electrochemical instruments. Thin-layer spectroelectrochemical measurements were performed with an IBM EC 225 voltammetric analyzer which was coupled with a Tracor Northern 1710 holographic optical spectrometer multichannel analyzer to obtain spectral data either as a function of

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(1) Sadasivon, N.; Fleischer, E. B. *J. Inorg. Nucl. Chem.* **1968**, *30*, 591.

(2) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Organomet. Chem.* **1978**, *159*, 317.

(3) Abbreviations: OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; TPP = 5,10,15,20-tetraphenylporphyrin dianion.

(4) Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.

(5) Del Rossi, K. J.; Wayland, B. B., personal communication.

(6) Collman, J. P.; Kim, K. *J. Am. Chem. Soc.* **1986**, *108*, 7847.

(7) Sugimoto, H.; Ueda, N.; Mori, M. *J. Chem. Soc., Dalton Trans.* **1982**, 1611.

(8) Cornillon, J.-L.; Anderson, J. E.; Swistak, C.; Kadish, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 7633.

0276-7333/87/2306-2146$01.50/0