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Multidentate Lewis Acids. Structure of the 1:2 Complex of a Bidentate Titanium Trichloroalkoxide with Pinacolone

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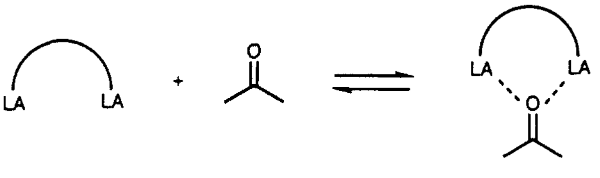
Summary: Treatment of the bis(trimethylsilyl) ether of racemic (1α,2β,3α)-3-methyl-1,2-cyclohexanediol with 2 equiv of TiCl$_4$ yields the titanium trichloroalkoxide **2**, a bidentate Lewis acid. An X-ray crystallographic study of its 1:2 complex with pinacolone has shown that the OTiCl$_3$ groups are equatorial and are doubly bridged by chloride, and each binds a single pinacolone to form an approximately octahedral complex. Compound **2** therefore incorporates dual acidic sites that allow two basic substrates to be bound in close proximity.

We have established that suitable bidentate Lewis acids can form complexes in which a carbonyl oxygen bridges both electrophilic sites (eq 1).[2,3] These complexes promise to be useful in synthesis because the carbonyl substrate is more susceptible to nucleophilic attack than when it is bound to simple monodentate Lewis acids.[4] Moreover, the stereochemistry of addition should be easier to control, since adducts of bidentate Lewis acids will have a more restricted range of conformations. During recent efforts to devise bidentate Lewis acids that exploit these advantages, we have found that the chiral zirconium trichloroalkoxide 1 and related compounds can be made easily from the corresponding diols.[5] Unfortunately, conformational mobility allows the OZrCl$_3$ groups of compound 1 to become diaxial and avoid engaging in cooperative binding.[5c] In this communication, we describe the behavior of a related compound in which two Lewis acidic sites maintain close proximity.



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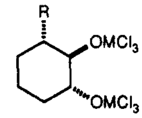

1 (R = H, M = Zr)
2 (R = CH$_3$, M = Ti)
3 (R = H, M = Ti)

Table I. Selected Interatomic Distances, Bond Angles, and Torsion Angles in the 1:2 Pinacolone Adduct of Bidentate Titanium Trichloroalkoxide 2

Distances (Å)

Ti(1)–Cl(1)	2.250 (3)	Ti(2)–Cl(3)	2.265 (3)
Ti(1)–Cl(2)	2.253 (3)	Ti(2)–Cl(4)	2.275 (3)
Ti(1)–Cl(5)	2.515 (3)	Ti(2)–Cl(5)	2.475 (3)
Ti(1)–Cl(6)	2.481 (3)	Ti(2)–Cl(6)	2.504 (3)
Ti(1)–O(1)	1.725 (6)	Ti(2)–O(2)	1.701 (5)
Ti(1)–O(11)	2.121 (6)	Ti(2)–O(41)	2.090 (5)

Bond Angles (deg)

Cl(1)–Ti(1)–Cl(2)	98.8 (1)	Cl(3)–Ti(2)–Cl(4)	98.8 (1)
Cl(1)–Ti(1)–Cl(5)	91.5 (1)	Cl(3)–Ti(2)–Cl(5)	92.4 (1)
Cl(1)–Ti(1)–Cl(6)	163.6 (1)	Cl(3)–Ti(2)–Cl(6)	168.7 (1)
Cl(1)–Ti(1)–O(1)	97.2 (2)	Cl(3)–Ti(2)–O(2)	96.1 (2)
Cl(1)–Ti(1)–O(11)	85.8 (2)	Cl(3)–Ti(2)–O(41)	87.3 (2)
Cl(2)–Ti(1)–Cl(5)	167.3 (1)	Cl(4)–Ti(2)–Cl(5)	164.8 (1)
Cl(2)–Ti(1)–Cl(6)	90.1 (1)	Cl(4)–Ti(2)–Cl(6)	89.1 (1)
Cl(2)–Ti(1)–O(1)	98.7 (2)	Cl(4)–Ti(2)–O(2)	98.4 (2)
Cl(2)–Ti(1)–O(11)	92.4 (2)	Cl(4)–Ti(2)–O(41)	86.4 (2)
Cl(5)–Ti(1)–Cl(6)	78.2 (1)	Cl(5)–Ti(2)–Cl(6)	78.5 (1)
Cl(5)–Ti(1)–O(1)	87.3 (2)	Cl(5)–Ti(2)–O(2)	90.6 (2)
Cl(5)–Ti(1)–O(11)	80.8 (2)	Cl(5)–Ti(2)–O(41)	83.7 (2)
Cl(6)–Ti(1)–O(1)	95.0 (2)	Cl(6)–Ti(2)–O(2)	90.8 (2)
Cl(6)–Ti(1)–O(11)	80.1 (2)	Cl(6)–Ti(2)–O(41)	85.1 (2)
O(1)–Ti(1)–O(11)	167.8 (3)	O(2)–Ti(2)–O(41)	173.6 (2)
Ti(1)–Cl(5)–Ti(2)	95.7 (1)	Ti(1)–Cl(6)–Ti(2)	95.8 (1)
Ti(1)–O(1)–C(1)	152.0 (5)	Ti(2)–O(2)–C(2)	164.7 (5)
Ti(1)–O(11)–C(11)	152.4 (6)	Ti(2)–O(41)–C(41)	147.8 (7)
		Ti(2)–O(51)–C(51)	148.7 (11)

Torsion Angles (deg)

Ti(1)–O(11)–C(11)–C(10)	31.7 (18)
Ti(1)–O(11)–C(11)–C(30)	-10.8 (22)
Ti(2)–O(41)–C(41)–C(40)	-36.7 (22)
Ti(2)–O(41)–C(51)–C(50)	33.4 (37)

Standard procedures[6] transformed racemic (1α,2β,3α)-3-methyl-1,2-cyclohexanediol[7] into the corresponding bis(trimethylsilyl) ether, which was then converted into the potentially bidentate titanium trichloroalkoxide 2 by the addition of 2 equiv of TiCl$_4$ at −78 °C.[8] Earlier studies have established that titanium trichloroalkoxides are typically monomeric in solution[9] and bind 2 equiv of ketones, giving *mer* octahedral complexes

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(1) Fellow of the Natural Sciences and Engineering Research Council of Canada, 1986–1990.

(2) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153–156.

(3) For other recent work on multidentate Lewis acids, see: Nadeau, F.; Simard, M.; Wuest, J. D. *Organometallics* **1990**, *9*, 1311–1314. Dohmeier, C.; Mattes, R.; Schnöckel, H. *J. Chem. Soc., Chem. Commun.* **1990**, 358–359. Kaufmann, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545–546. Chujo, Y.; Tomita, I.; Saegusa, T. *Macromolecules* **1990**, *23*, 687–689. Layh, M.; Uhl, W. *Polyhedron* **1990**, *9*, 277–282. Jurkschat, K.; Rühlemann, A.; Tzschach, A. *J. Organomet. Chem.* **1990**, *381*, C53–C56. Kelly, T. R.; Meghani, P. *J. Org. Chem.* **1990**, *55*, 3684–3688. Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 2422–2424. Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294–6301. Jurkschat, K.; Kuivila, H. G.; Liu, S.; Zubieta, J. A. *Organometallics* **1989**, *8*, 2755–2759. Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179–2183. Schmidbaur, H.; Öller, H.-J.; Wilkinson, D. L.; Huber, B.; Müller, G. *Chem. Ber.* **1989**, *122*, 31–36. Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297–300. Kaufmann, D. *Chem. Ber.* **1987**, *120*, 901–905. Khan, M. A.; Peppe, C.; Tuck, D. G. *Organometallics* **1986**, *5*, 525–530.

(4) Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1985**, *107*, 6121–6123.

(5) (a) Sharma, V.; Simard, M.; Wuest, J. D. *Inorg. Chem.*, submitted for publication. (b) Bélanger-Gariépy, F.; Hoogsteen, K.; Sharma, V.; Wuest, J. D. *Inorg. Chem.*, submitted for publication. (c) Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 955–958. (d) Galeffi, B.; Simard, M.; Wuest, J. D. *Inorg. Chem.* **1990**, *29*, 951–954.

(6) Lasocki, Z. *Synth. Inorg. Met-Org. Chem.* **1973**, *3*, 29–35.

(7) Lepoittevin, J.-P.; Benezra, C. *J. Med. Chem.* **1986**, *29*, 287–291. Robinson, P. L.; Evans, S. A., Jr. *J. Org. Chem.* **1985**, *50*, 3860–3863. Klein, J.; Dunkelblum, E. *Tetrahedron* **1968**, *24*, 5701–5710.

(8) For a related reaction, see: Kunz, H.; Müller, B.; Schanzenbach, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 267–269.

(9) Martin, R. L.; Winter, G. *J. Chem. Soc.* **1961**, 2947–2957. Rasuwajew, G. A.; Bobinowa, L. M.; Etlis, V. S. *Tetrahedron* **1959**, *6*, 154–160. Bradley, D. C.; Hancock, D. C.; Wardlaw, W. *J. Chem. Soc.* **1952**, 2773–2778.

0276-7333/90/2309-2860$02.50/0

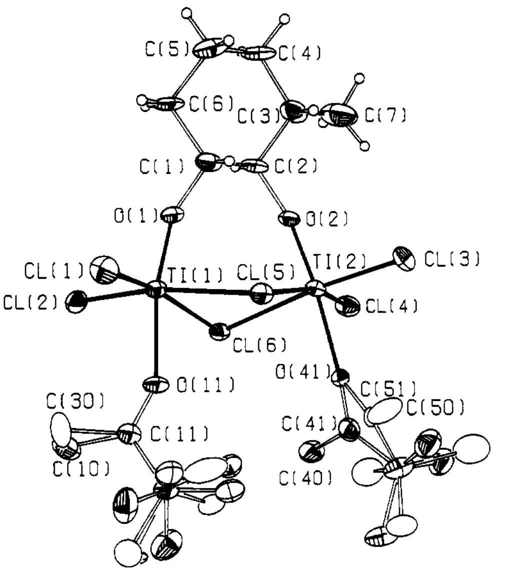

Figure 1. ORTEP drawing of the structure of the 1:2 pinacolone adduct of bidentate titanium trichloroalkoxide **2**. The ellipsoids correspond to 33% probability, and selected hydrogen atoms are shown as spheres of arbitrary size.

in which one ligand is trans to the alkoxy group.[5c,10,11] We hoped that the methyl group in compound **2** would impose an all-equatorial conformation and thereby force the Lewis acidic sites together, preventing them from binding the normal complement of four ligands and ensuring cooperative behavior. In fact, addition of 4 equiv of 3,3-dimethyl-2-butanone (pinacolone) and then pentane to a suspension of compound **2** in toluene produced an 81% yield of crystals of a complex containing only 2 equiv of pinacolone.[12] A similar procedure also converted the analogue **3** into a crystalline 1:2 pinacolone complex, demonstrating that the methyl group does not actually play a crucial role.

An X-ray crystallographic study revealed that the 1:2 adduct of compound **2** has the partially disordered structure shown in Figure 1.[13] Selected interatomic distances, bond angles, and torsion angles are listed in Table I. These data confirm that the cyclohexane ring adopts a normal chair conformation with equatorial $OTiCl_3$ groups. These groups are doubly bridged by chloride, and each binds a single pinacolone to form an approximately octahedral complex. Each ketone is trans to an alkoxy group and is primarily σ-bonded. The average lengths of terminal Ti–Cl bonds (2.261 (3) Å), bridging Ti–Cl bonds (2.494 (3) Å), alkoxy Ti–O bonds (1.713 (5) Å), and carbonyl Ti···O bonds (2.106 (6) Å) are closely similar to those found in related compounds.[14,15] Furthermore, strong oxygen p–titanium d π-bonding helps produce a typically large average alkoxy C–O–Ti angle (158.4 (5)°) and carbonyl C=O···Ti angle (150.2 (11)°).[16] In general, the structure resembles those of dimeric, chloride-bridged 1:1 adducts of $TiCl_4$ with esters except that bidentate acid **2** forces substrates to be bound on the same side of the approximate Ti_2Cl_6 plane.[15]

The crystalline 1:2 pinacolone complex of titanium trichloroalkoxide **2** was dissolved in CD_2Cl_2 to give a solution of nominal 0.13 M concentration. At −85 °C, its ^1H and ^{13}C NMR spectra showed the presence of a single major species with equatorial substituents and two nonequivalent bound pinacolones. Small amounts (~5%) of the 1:2 adduct of $TiCl_4$ with pinacolone could also be detected. These observations suggest that complexes of the bidentate titanium trichloroalkoxide **2** have similar structures in solution and in the solid state but that some redistribution occurs in solution, particularly at low concentrations.

Although the adjoining $OTiCl_3$ groups of compound **2** do not in fact engage in cooperative binding of ketones, their interaction via chloride bridging creates dual acidic sites that allow two bases to be bound in close proximity. This novel juxtaposition may allow compound **2** to act as a host for suitable bidentate guests or as an effective template for the reductive coupling of carbonyl compounds[17] or for the photodimerization of α,β-enones.[18] We are also exploring the possibility that carbonyl compounds less hindered or more basic than pinacolone may in fact bridge both Lewis acidic sites.

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(10) Bachand, B.; Wuest, J. D. Unpublished observations.

(11) For related studies of complexes of $TiCl_4$ with ketones, see: Turin, E.; Nielson, R. M.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *134*, 67–78, 79–85. Marcos, B.; Amaudrut, J.; Devin, C. *J. Chem. Res., Miniprint* **1977**, 1901–1914.

(12) The crystals consist of bidentate titanium trichloroalkoxide **2**, pinacolone, and toluene in a 1:2:0.5 ratio: mp 95–115 °C dec; IR (Nujol mull) 1655, 1140, 1085, 1045, 1030, 730, 395, 350 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.11 (m, 1 H), 1.29 (s, 18 H), 1.30 (m, 2 H), 1.41 (d, 3 H), 1.74 (m, 3 H), 2.00 (m, 1 H), 2.36 (s, toluene), 2.65 (s, 6 H), 4.99 (t, 1 H), 5.45 (m, 1 H), 7.15–7.30 (m, toluene); ^{13}C NMR (75.4 MHz, CD_2Cl_2, 0 °C) δ 18.52, 21.60, 22.60, 26.06, 26.28, 31.69, 32.37, 38.98, 47.07, 100.33, 106.09, 125.43, 128.36, 129.17, 138.16, 232.64. Anal. Calcd for $C_{19}H_{36}Cl_6O_4Ti_2 \cdot 0.5C_7H_8$: C, 39.56; H, 5.91. Found: C, 39.43; H, 6.03.

(13) (a) Crystallographic data: triclinic, space group $P\bar{1}$, a = 11.381 (6) Å, b = 12.186 (15) Å, c = 13.054 (15) Å, α = 75.92 (10)°, β = 76.46 (14)°, γ = 68.99 (14)°, V = 1617.6 Å^3, d_{calc} = 1.402 g cm^{-3}, and Z = 2. An Enraf-Nonius CAD-4 diffractometer was used to collect 5684 independent reflections at 173 K with Mo K$\bar{\alpha}$ radiation (λ = 0.710 69 Å). Full-matrix least-squares refinement of 2949 reflections ($I \geq 3.00\sigma(I)$) converged at R = 0.060 and R_w = 0.046. Corrections were applied for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods (SHELXS86) and difference-Fourier calculations (SHELX76). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares procedures. (b) The toluene of crystallization is partially disordered and is not shown in Figure 1. Disordered models were used to describe both bound pinacolones. In one, three sets of methyl carbons attached to C(12) were defined and assigned occupancies of 0.33, and two methyl carbons attached to C(11) were refined and fixed at occupancies of 0.66 (C(10)) and 0.33 (C(30)). In the other pinacolone, peaks around C(42) were grouped into two sets defining reasonable *tert*-butyl groups. Peaks corresponding to the remaining carbon atoms were also grouped into two sets (C(40), C(41) and C(50), C(51)) that gave refined populations of 0.66 and 0.33, respectively.

(14) Albanese, J. A.; Staley, D. L.; Rheingold, A. L.; Burmeister, J. L. *Inorg. Chem.* **1990**, *29*, 2209–2213. Troyanov, S. I.; Mach, K. *J. Organomet. Chem.* **1990**, *389*, 41–46. Riediker, M.; Hafner, A.; Piantini, U.; Rihs, G.; Togni, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 499–500. Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66–67. Oppolzer, W.; Rodriguez, I.; Blagg, J.; Bernardinelli, G. *Helv. Chim. Acta* **1989**, *72*, 123–130. Utko, J.; Sobota, P.; Lis, T. *J. Organomet. Chem.* **1987**, *334*, 341–345. Maier, G.; Seipp, U.; Boese, R. *Tetrahedron Lett.* **1987**, *28*, 4515–4516. Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 610–611. Poll, T.; Metter, J. O.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 112–114. Haase, W.; Hoppe, H. *Acta Crystallogr., Sect. B* **1968**, *B24*, 281–282. Watenpaugh, K.; Caughlan, C. N. *Inorg. Chem.* **1966**, *5*, 1782–1786.

(15) Bassi, I. W.; Calcaterra, M.; Intrito, R. *J. Organomet. Chem.* **1977**, *127*, 305–313. Brun, L. *Acta Crystallogr.* **1966**, *20*, 739–749.

(16) For references, see: Huffman, J. C.; Moloy, K. G.; Caulton, K. G. *Inorg. Chem.* **1988**, *27*, 2190–2192. Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, Chapter 15.3. Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995–1001.

(17) For recent references, see: Pons, J.-M.; Santelli, M. *J. Org. Chem.* **1989**, *54*, 877–884.

(18) Lewis, F. D.; Barancyk, S. V. *J. Am. Chem. Soc.* **1989**, *111*, 8653–8661. Ogawa, T.; Masui, Y.; Ojima, S.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 423–425.

ture ^1H and ^{13}C NMR spectra.

Registry No. 2, 129493-36-3; $2 \cdot 2$(pinacolone)$\cdot ^1/_2C_7H_8$, 129493-40-9; 3, 129493-37-4; $3 \cdot 2$(pinacolone), 129493-38-5; $TiCl_4 \cdot 2$(pinacolone), 129493-41-0; (±)-(1α,2β,3α)-3-methyl-1,2-cyclohexanediol[bis(trimethylsilyl ether)], 129493-35-2.

Supplementary Material Available: Tables containing atomic coordinates and equivalent isotropic temperature factors, complete bond lengths and angles, anisotropic thermal parameters, and fixed hydrogen atom coordinates (9 pages); a table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Deprotonation of a Cp* Methyl Group by an Iridium Anilide: Formation, Structure, and Solution Dynamics of an η^4-Tetramethylfulvene Complex

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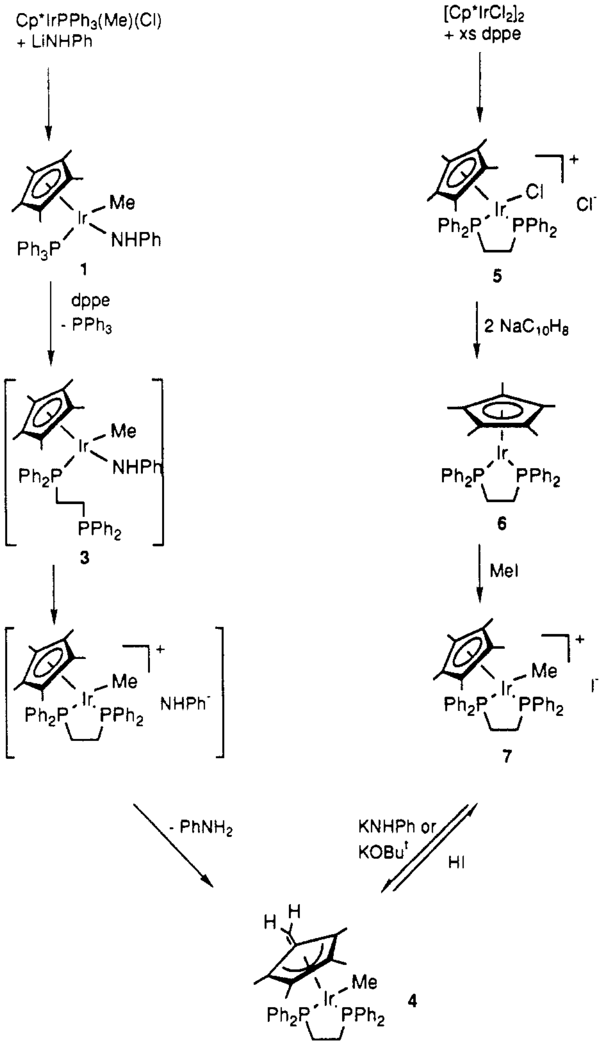
Summary: The new iridium amide complex Cp*IrPPh$_3$(Me)(NHPh) (**1**, Cp* = η^5-C_5Me_5) reacts with 1,2-bis(diphenylphosphino)ethane (dppe) to give PPh$_3$, aniline, and the tetramethylfulvene complex (η^4-$C_5Me_4CH_2$)Ir(dppe)Me (**4**), which has been characterized by X-ray crystallography and by variable-temperature NMR spectroscopy. Deprotonation of [Cp*Ir(dppe)Me]$^+$I$^-$ (**7**) with KNHPh or KOBu^t also gives **4**, suggesting that the anilide ligand is displaced from **1** as an anion, which immediately deprotonates a Cp* methyl group. The fact that deprotonation of **7**-d_3 (prepared from Cp*Ir(dppe) (**6**) and CD_3I) gives **4**-d_3 demonstrates that the Cp* methyl is the kinetic site of deprotonation even though it is more remote than the Ir-bound methyl from the positively charged metal center.

We report the synthesis of the amide complex Cp*IrPPh$_3$(Me)(NHPh) (1, Scheme I, Cp* = η^5-C_5Me_5) and its unusual reaction with 1,2-bis(diphenylphosphino)ethane (dppe) to form (η^4-$C_5Me_4CH_2$)Ir(dppe)Me (4), the first structurally characterized example of an η^4-tetramethylfulvene complex.[1] The anilide ligand in 1 appears to be displaced as an anion, which selectively deprotonates a Cp* methyl group to give 4.

Reaction of Cp*IrPPh$_3$(Me)(Cl)[2] with LiNHPh in THF at 85 °C for 3–4 h gives 1 in 80% yield. Anilide 1 reacts with PPh$_2$Me to give PPh$_3$ and Cp*Ir(PPh$_2$Me)(Me)(NHPh) (2).[3] When 1 is treated with the chelating phosphine dppe in C_6D_6 or toluene-d_8, PPh$_3$, aniline, and the title complex 4 are formed; a transient species, presumably Cp*Ir(η^1-dppe)(Me)(NHPh) (3, Scheme I) appears to be an intermediate. After 1 h the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows two doublets (J_{P-P} = 33 Hz) assigned to 3, one at δ 5.5 (coordinated P) and the other at δ −9.8 (dangling P), in addition to signals due to PPh$_3$, 1, and 4. After 24 h compounds 1 and 3 are consumed and the NMR spectra show only the fulvene complex 4 and aniline. Compound 4 can be separated from PPh$_3$ by fractional crystallization and isolated as orange crystals in 50–75% yield.

Scheme I



The crystal structure[4] of 4 (an ORTEP diagram is shown in Figure 1) demonstrates that the Cp* has been depro-

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(1) For leading references to examples of fulvene η^6 coordination, see: (a) Kolle, U.; Kang, B.-S.; Thewalt, U. *J. Organomet. Chem.* **1990**, *386*, 267. (b) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (c) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (d) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* **1985**, 945. (e) For tetramethylfulvene bridging two metals see: Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Yan, X.; Nagelkerke, R.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1424. Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703. (f) For an example of η^4 coordination, see: Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053. (g) For η^2 coordination, see: Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H.-J.; Kruger, C. *Organometallics* **1983**, *2*, 1369.

(2) Prepared analogously to the PMe$_3$ complex: Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. Full details will be reported separately.[3]

(3) Glueck, D. S.; Bergman, R. G. Submitted for publication.

(4) Crystals were grown from toluene/hexamethyldisiloxane at 20 °C. Crystal data for 4: $C_{37}H_{41}IrP_2$, $I2/a$, V = 6304 (3) Å^3, Mo Kα (λ = 0.70926 Å), μ_{calc} = 43.4 cm^{-1}, d_{calc} = 1.56 g cm^{-3}, a = 20.625 (4) Å, b = 17.188 (3) Å, c = 17.810 (3) Å, β = 93.14 (2)°, T = 101 °C, Z = 8, $2\theta_{max}$ = 45°. The final residuals for 176 variables refined against the 3025 data for which $F^2 > 3\sigma(F^2)$ were R = 3.8%, R_w = 4.5%, and GOF = 1.67. The R value for all 4109 data was 6.1%. Details of the structure determination are provided as supplementary information.

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