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

Registry No. 2, 129493-36-3; 2·2(pinacolone)·$^1/_2$C$_7$H$_8$, 129493-40-9; 3, 129493-37-4; 3·2(pinacolone), 129493-38-5; TiCl$_4$·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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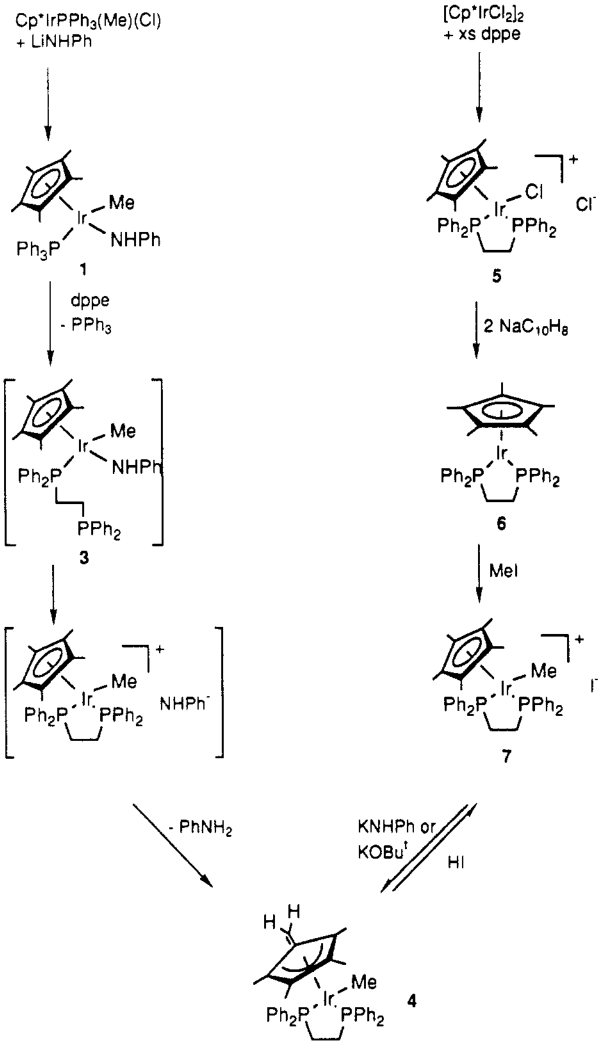
Summary: The new iridium amide complex Cp*IrPPh$_3$(Me)(NHPh) (**1**, Cp* = η^5-C$_5$Me$_5$) reacts with 1,2-bis(diphenylphosphino)ethane (dppe) to give PPh$_3$, aniline, and the tetramethylfulvene complex (η^4-C$_5$Me$_4$CH$_2$)Ir(dppe)Me (**4**), which has been characterized by X-ray crystallography 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$_3$I) 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$_5$Me$_5$) and its unusual reaction with 1,2-bis(diphenylphosphino)ethane (dppe) to form (η^4-C$_5$Me$_4$CH$_2$)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.

Scheme I



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$_6$D$_6$ 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{^{1}H} 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.

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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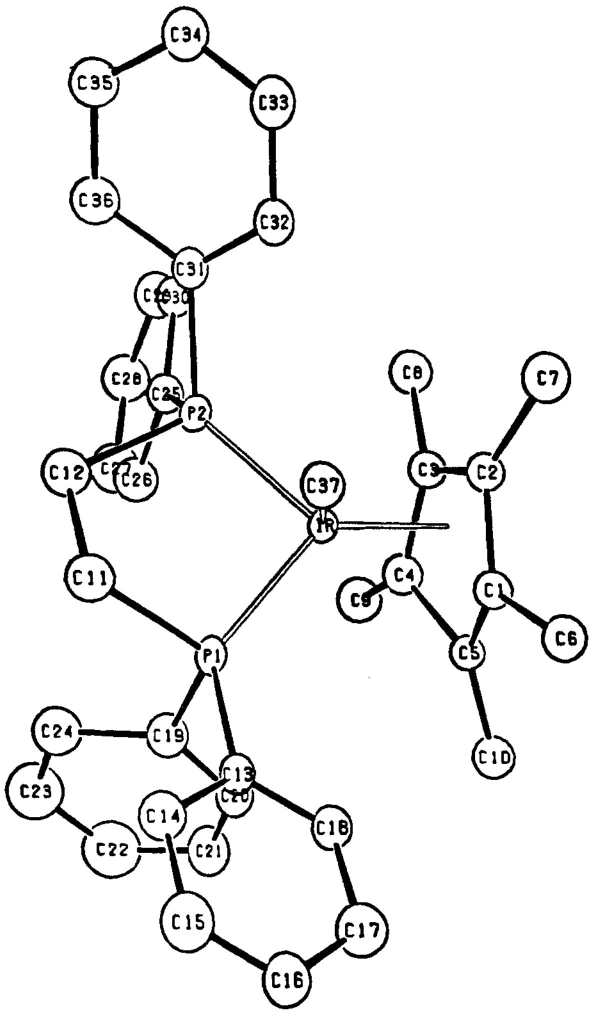

Figure 1. ORTEP drawing of (η^4-$C_5Me_4CH_2$)Ir(dppe)Me (4). The Ir and P atoms were refined anisotropically; all other atoms were refined isotropically. The ellipsoids and spheres in the drawing represent the 50% probability surface for each atom. Selected bond distances (Å): Ir–C_1 = 2.204 (8); Ir–C_2 = 2.172 (8); Ir–C_3 = 2.204 (8); Ir–C_4 = 2.285 (8); Ir–C_5 = 2.635 (7); C_1–C_2 = 1.478 (11); C_1–C_5 = 1.478 (11); C_2–C_3 = 1.425 (11); C_3–C_4 = 1.426 (11); C_4–C_5 = 1.470 (11); C_5–C_{10} = 1.377 (10); Ir–C_{37} = 2.151 (8); Ir–P_1 = 2.278 (2); Ir–P_2 = 2.265 (2).

tonated and the resulting fulvene ligand is bound in an η^4 fashion. The distance from the metal to the four bonded ring carbons C_1–C_4 ranges from 2.285 (8) to 2.172 (8) Å, and the Ir–C_5 distance is 2.635 (7) Å. The methylene ring carbon is bent away from the metal and displaced from the C_1–C_4 plane by 0.40 (1) Å. The methylene C–C distance is 1.38 (1) Å, and the ring C–C bond lengths range from 1.425 (11) to 1.478 (11) Å. An IR absorption (1594 cm^{-1} (KBr); 1598 cm^{-1} (C_6H_6)) can be assigned to the methylene C=C stretch[5] and suggests that the solid-state structure is maintained in solution.

The NMR spectra of 4 are temperature-dependent. At 20 °C in THF-d_8, in addition to signals due to coordinated dppe and the Ir–Me group (δ −0.87, t, J = 6.6 Hz), a triplet resonance at δ 2.29 (2 H, J = 4.0 Hz, CH_2) and signals at δ 1.71 and 0.98 (6 h each) due to the methyl groups of the tetramethylfulvene are observed. At −75 °C, these methyls become inequivalent and give rise to four signals at δ 1.87, 1.41, 1.10, and 0.79. The CH_2 protons now appear as two peaks at δ 2.37 and 2.26. Similarly, at 20 °C only a broad signal at δ 23.8 can be observed in the $^{31}P\{^1H\}$ NMR spectrum; at −70 °C two doublets (J_{P-P} = 43.9) at δ 27.9 and 18.2 are resolved. At 20 °C, the $^{13}C\{^1H\}$ NMR spectrum in toluene-d_8 shows signals due to the methylene group[6] at δ 67.9 (t, J_{P-C} = 7.0 Hz, CH_2=C) and at δ 159.1 (C=CH_2), but resonances from the remaining ring carbons of the fulvene are not resolved. At −75 °C, these peaks can be observed as four separate signals in the range δ 97.9–58.8. These reversible spectral changes are consistent with rotation of the fulvene ligand about the Ir–fulvene axis.[7] At ambient temperature, this process is rapid on the NMR time scale, making equivalent the two phosphorus atoms and the two sets of ring methyl groups. At low temperature the rotation is slower and the NMR spectra are consistent with a structure identical with that found in the solid state. The symmetric structure formed by 90° rotation of the fulvene, making the Ir—Me and C=CH_2 vectors parallel, is apparently disfavored by steric interactions of the fulvene methyls with the dppe phenyl groups.

Fulvene complex 4 was independently synthesized by deprotonation of the cation [Cp*Ir(dppe)Me]$^+$ as shown in Scheme I. Treatment of [Cp*$IrCl_2$]$_2$ with excess dppe in CH_2Cl_2 at 85 °C for 1 day gives the salt [Cp*Ir(dppe)Cl]$^+$Cl$^-$ (5),[8] which can be reduced with sodium naphthalenide in THF to give neutral Cp*Ir(dppe) (6). Methylation of 6 with MeI in THF yields [Cp*Ir(dppe)Me]$^+$I$^-$ (7). As predicted by the proposed mechanism for the formation of 4, 7 is readily deprotonated by KNHPh or KOBu^t in THF to give 4.[9] Treatment of 4 with HI(aq) regenerates the cation 7. Deprotonation of 7-d_3 (prepared from 6 and CD_3I) gives 4-d_3, suggesting that protons are not removed from the iridium-bound methyl group before the final product is formed. While deprotonation of methyl groups attached to cationic metal centers can lead to alkylidenes,[10] this work and a recent study from Bercaw's laboratory[1f] indicate that when Cp* and metal-bound methyl groups are both present, the Cp* methyl can be the the kinetic site of deprotonation even though it is more remote from the positively charged metal center.

Acknowledgment. This work was supported by the National Institutes of Health through Grant GM-25459. We thank Johnson-Matthey for a loan of $IrCl_3 \cdot 3H_2O$, Dr. F. J. Hollander for solving the crystal structure, and Professor John Bercaw for helpful discussions.

Supplementary Material Available: Experimental details and spectroscopic data for compounds 1 and 4–7 and X-ray structure details for 4, including tables of crystal data, positional and thermal parameters, and bond distances and angles (13 pages); a table of structure factors for 4 (24 pages). Ordering information is given on any current masthead page.

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(5) See ref 1f and: Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*; McGraw-Hill: London, 1980; p 61.

(6) Confirmed by DEPT experiments. For C=CH_2, J_{CH} = 155.5 Hz. The four-bond coupling to P observed in both the ^{13}C and ^1H NMR spectra of the methylene group is surprisingly large.

(7) Probitts, E. J.; Mawby, R. J. *J. Organomet. Chem.* **1986**, *310*, 121. As a reviewer has noted, our data do not distinguish between simple rotation about this axis and a more complicated process involving η^4 to η^2 isomerization of the fulvene ligand following by 90° rotation.

(8) For the analogous Rh complex, see: Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(9) Deprotonation of Cp* and hexamethylbenzene methyl groups has been observed; for leading references see: Gloaguen, B.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 4607. Moulines, F.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 614.

(10) See for example: (a) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389. (b) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.