The Binuclear Iridium(II) Hydride Complex $[(C_5Me_5)Ir(\mu\text{-H})]_2$: A Novel Base for Reversible Deprotonation of Acidic Organic Compounds and a Unique Catalyst for C−C Bond Cleavage of Aromatic 1,2-Diols and Michael Additions

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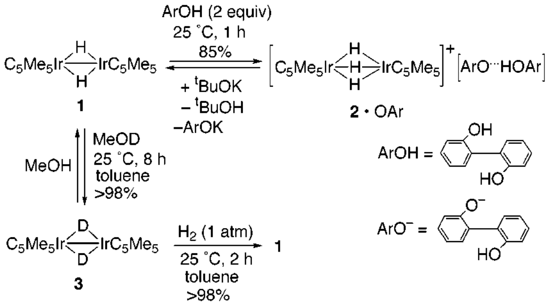
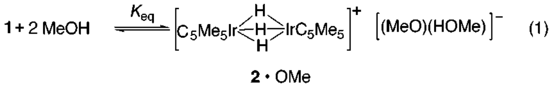
Transition-metal hydride complexes bearing the pentamethylcyclopentadienyl (C_5Me_5) ligand are of particular interest and importance in organometallic chemistry and homogeneous catalysis. For iridium hydride complexes bearing the C_5Me_5 ligand, a number of complexes in the oxidation states of +3, +4, and +5 have been synthesized and have had their reactivity studied in the past three decades.[1,2] However, this type of complex in the +2 oxidation state, the lowest accessible and possibly the most reactive one in this series of complexes, has hardly been explored.[1] During our recent studies on transition-metal ketyl complexes, we serendipitously isolated and structurally characterized a binuclear iridium(II) dihydride complex, $[(C_5Me_5)Ir(\mu\text{-H})]_2$ (**1**),[3] which, as far as we are aware, represents the first example of a well-defined (pentamethylcyclopentadienyl)iridium(II) hydride complex. We have now found that this Ir(II) complex **1** is a unique metal hydride complex which shows an unprecedented versatile reactivity toward a variety of substrates. Among its most remarkable reactions is proton abstraction from acidic organic compounds to yield *reversibly* the corresponding metal-protonated cationic species $\{[(C_5Me_5)Ir]_2(\mu\text{-H})_3\}^+$ (**2**). The *reversible* protonation/deprotonation character makes **1** a unique *catalyst* for C−C bond cleavage of aromatic 1,2-diols and Michael additions. Described herein are some representative results.

Although an apparent reaction between **1** and MeOH was not observed at 25 °C in toluene-d_8 or CD_2Cl_2 by ^1H NMR, the reaction of **1** with MeOD (ca. 200 equiv) under similar conditions yielded almost quantitatively the corresponding deuteride complex **3** (Scheme 1). Treatment of **3** with MeOH or H_2 (1 atm) at room-temperature regenerated **1** almost quantitatively (Scheme 1).[4] When the mixture of **1** and MeOH was cooled to −30 °C, two new signals with the proton ratio of 30 to 3 appeared at δ 1.66 (C_5Me_5) and −15.38 (Ir−H) in toluene-d_8 or δ 2.01 and −15.55 in CD_2Cl_2, respectively, in addition to the peaks for **1**.[3] These new signals could be compared with those previously reported for the dimeric trihydridoiridium cation species $\{[(C_5Me_5)Ir]_2(\mu\text{-H})_3\}^+(PF_6)^-$ (**2**·PF_6) (δ 2.09, −15.33 in $CDCl_3$),[2a,5] suggesting that a similar cationic species such as $\{[(C_5Me_5)Ir]_2(\mu\text{-H})_3\}^+[(OMe)(HOMe)_n]^-$ (**2**·OMe) might be formed in the present reaction.[6] The new signals assignable to the cationic species became stronger as the temperature was decreased, but disappeared upon warming up to room temperature, which suggests that the formation of the cationic species such as **2**·OMe must be reversible. Suppose that the methoxide anion in **2**·OMe was stabilized by one molecule of MeOH (n = 1, vide infra), an equilibrium constant of $K_{eq} = 1.02 \times 10^{-2}$ for the reaction of **1** with MeOH in toluene-d_8 at 25 °C (eq 1) could be estimated from the van't Hoff equation ($\Delta H = -18.26$ kJ mol^{-1}, $\Delta S = -99.35$ J mol^{-1} K^{-1}).

Scheme 1





Although isolation of the cationic species **2**·OMe from **1** and MeOH was difficult, an analogous reaction of **1** with 2 equiv of 2,2′-biphenol in toluene afforded the corresponding cationic complex **2**·OAr (OAr = 2-(2′-hydroxyphenyl)phenoxide) in 85% isolated yield, in which the aryloxide counteranion was stabilized by interaction with one molecule of 2,2′-biphenol as confirmed by an X-ray diffraction study (Scheme 1).[7] When **2**·OAr was treated with 4 equiv of ᵗBuOK in CH_2Cl_2, the neutral complex **1** was recovered almost quantitatively, which clearly shows that the cationic unit $\{[(C_5Me_5)Ir]_2(\mu\text{-H})_3\}^+$ in **2**·OAr is protonic and can be deprotonated by an appropriate base.

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(1) Reviews: (a) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (b) Leigh, G. J.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 5, p 541. (c) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81. (d) Bergman, R. G. *J. Organomet. Chem.* **1990**, *400*, 273. (e) Atwood, J. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Atwood, J. D., Eds.; Pergamon: Oxford, 1995; Vol. 8, p 303. (f) Bianchini, C. Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109.

(2) For examples, see: (a) White, C.; Oliver, A. J., Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1901. (b) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3502. (c) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508. (d) Grushin, V. V.; Vymenits, A. B.; Yanovsky, A. I.; Struchkov, Y. T.; Vol'pin, M. E. *Organometallics* **1991**, *10*, 48. (e) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198. (f) Vicic, D. A.; Jones, W. D. *Organometallics* **1997**, *16*, 1912.

(3) Hou, Z.; Fujita, A.; Koizumi, T.; Yamazaki, H.; Wakatsuki, Y. *Organometallics* **1999**, *18*, 1979.

(4) Monitoring of the reaction of **1** with MeOD and that of **3** with MeOH or H_2 by ^1H or ^2H NMR suggested the formation of a monohydride/monodeuteride species such as $[(C_5Me_5)Ir]_2(\mu\text{-H})(\mu\text{-D})$ (δ −13.42, Ir−H/D) at the early stage of the reaction. This is the only observable intermediate at room temperature. A longer-time (>10 h) reaction of **3** with H_2 afforded the known Ir(IV) complex $[(C_5Me_5)IrH_3]_2$[2c,e] together with some unidentified hydride species.

(5) For structural characterization of $\{[(C_5Me_5)Ir]_2(\mu\text{-H})_3\}^+(A)^-$ (A = BF_4 or ClO_4), see: (a) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176. (b) Stevens, R. C.; Mclean, M. R.; Wen, T.; Carpenter, J. D.; Bau, R.; Koetzle, T. F. *Inorg. Chim. Acta* **1989**, *161*, 223.

(6) For previous examples of protonation of transition-metal hydride complexes, see: (a) Kristjánsdóttir, S. S.; Norton, J. R. Acidity of Hydrido Transition Metal Complexes in Solution. In *Transition Metal Hydrides*; Dedieu, A. Ed.; VCH: New York, 1991; pp 309−359. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (c) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (d) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (e) Kubas G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (f) Papish, E. T.; Rix, F. C.; Spetseris, N.; Norton, J. R.; Williams, R. D. *J. Am. Chem. Soc.* **2000**, *122*, 12235 and references therein.

(7) Crystallographic data for **2**·OAr: orthorhombic, space group $Pca2_1$ (No. 29), a = 20.165(7) Å, b = 8.580(3) Å, c = 22.964(8) Å, V = 3973(2) Å^3, Z = 4, D_c = 1.711 g cm^{-3}, μ(Mo Kα) = 67.31 cm^{-1}, R (R_w) = 0.0513 (0.0982) for 3974 unique data with $I > 2\sigma(I)$ and 451 parameters. ^1H NMR (CD_2Cl_2, 25 °C): δ 12.82 (br s, 3H, OH), 6.77−7.35 (m, 16 H, aromatic), 2.01 (s, 30H, C_5Me_5), −15.57 (s, 3 H, Ir−H). Anal. Calcd for $C_{44}H_{44}Ir_2O_4$: C, 51.34; H, 5.09. Found: C, 51.15; H, 5.05.

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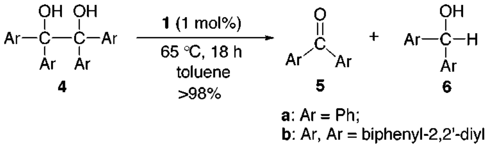
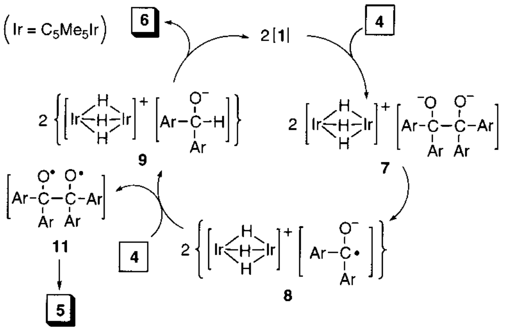
Scheme 2



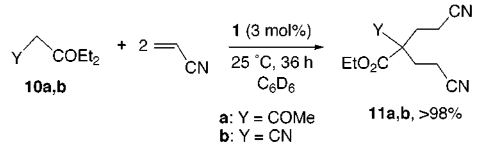
More remarkably, when **1** was stirred with 1 equiv of benzopinacol in toluene-d_8 at room temperature for 6 h, benzophenone and benzhydrol, that is, the C−C bond cleavage products of benzopinacol, were obtained almost quantitatively, while **1** remained unchanged as confirmed by the ^{1}H NMR spectrum. This reaction could be achieved *catalytically*. In the presence of 1 mol % of **1**, benzopinacol (**4a**) was transformed almost quantitatively to benzophenone (**5a**) and benzhydrol (**6a**) at 65 °C within 18 h (Scheme 2). The use of 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diol (**4b**) in place of benzopinacol afforded fluorenone (**5b**) and fluorenol (**6b**) analogously. Although formation of a ketyl species by deprotonation and C−C bond cleavage of a 1,2-diol has been previously reported,[8a−c,e] the *catalytic* separation of a 1,2-diol into a pair of ketone and alcohol is, to the best of our knowledge, unprecedented.[9] These reactions could be explained by the mechanism shown in Scheme 3, in which the protonation of **1** by the 1,2-diol **4** to give the 1,2-diolate **7** and the intramolecular deprotonation of the cationic unit in **9** to release **1** and the alcohol **6** play a crucially important role in the catalytic cycle.[8,10]

Complex **1** could also reversibly abstract a proton from active methylene compounds and act as a catalyst for Michael addition reactions. The reaction of **1** with 1 equiv of $CH_2(COCF_3)_2$ in THF gave the structurally characterizable cationic complex $\{[(C_5Me_5)Ir]_2(\mu\text{-}H)_3\}^+[CH(COCF_3)_2]^-$ ($\mathbf{2}\cdot CH(COCF_3)_2$) in 78% isolated yield.[11] In the presence of 3 mol % of **1**, the reaction of ethyl acetoacetate (**10a**) or ethyl cyanoacetate (**10b**) with 2 equiv of acrylnitrile at room temperature afforded almost quantitatively the addition product **11a** or **11b**, respectively (Scheme 4). These reactions represent a rare example of catalytic Michael addition under neutral conditions.[12]

Scheme 3



Scheme 4



In summary, we have found that the binuclear iridium(II) hydride complex **1** is a novel base for *reversible* deprotonation of acidic organic compounds, leading to unprecedented *catalytic* C−C bond cleavage of aromatic 1,2-diols and *catalytic* Michael addition under neutral conditions. Further studies on the reactivity of **1** are under progress.

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Supporting Information Available: A listing of atomic coordinates, thermal parameters, bond distances and angles, and ORTEP drawings for $\mathbf{2}\cdot$OAr and $\mathbf{2}\cdot CH(COCF_3)_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] The elementary steps, which correspond to the C−C bond cleavage of the 1,2-diolate **7** to give the ketyl species **8**,[8a−c,e] the hydrogen radical (H$^\bullet$) abstraction of the ketyl radical **8** from the 1,2-diol **4** to yield **9** and **11**,[8a,b,d] and the homolytic cleavage of the central C−C bond in **11** to give the ketone **5**[8b,d] in Scheme 3, have been described previously. (a) Hou, Z.; Jia, X.; Fujita, A.; Tezuka, H.; Yamazaki, H.; Wakatsuki, Y. *Chem. Eur. J.*, **2000**, *6*, 2994. (b) Hou, Z.; Fujita, A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754. (c) Hou, Z.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 2503. (d) Hou, Z.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7843. (e) Hou, Z.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1995**, *117*, 4421.

[9] Oxidation of aromatic 1,2-diols to give the corresponding ketones has been previously reported. For examples, see: (a) Bockman, T. M.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6542. (b) Han, D. S.; Shine, H. J. *J. Org. Chem.* **1996**, *61*, 3977. (c) Penn, J. H.; Duncan, J. H. *J. Org. Chem.* **1993**, *58*, 2003. (d) Perrier, S.; Sankararaman, S.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1993**, 825.

[10] Some processes such deprotonation and the C−C bond cleavage of the 1,2-diolate **7** to give **8** in Scheme 3 are reversible (see also ref 8). However, the reverse steps in Scheme 3 were omitted for clarity.

[11] Crystallographic data for $\{[(C_5Me_5)Ir]_2(\mu\text{-}H)_3\}^+[CH(COCF_3)_2]^-\cdot$THF: monoclinic, space group $C2/c$ (No. 15), $a = 16.551(5)$ Å, $b = 17.307(4)$ Å, $c = 13.311(8)$ Å, $\beta = 118.116(8)°$, $V = 3363(2)$ Å^3, $Z = 4$, $D_c = 1.851$ g cm^{-3}, μ(Mo Kα) = 79.87 cm^{-1}, R (R_w) = 0.0552 (0.0867) for 2635 unique data with $I > 3\sigma(I)$ and 182 parameters. ^{1}H NMR (C_6D_6, 25 °C): δ 6.23 (s, 1 H, $CH(COCF_3)_2$), 1.60 (s, 30 H, C_5Me_5), −15.37 (s, 3 H, Ir−H). Anal. Calcd for $C_{25}H_{34}Ir_2O_2F_6$: C, 34.71; H, 3.96. Found: C, 35.01; H, 4.03.

[12] For examples of catalytic Michael reactions under neutral conditions, see: (a) Murahashi, S.-I.; Naota, T.; Taki, H.; Mizuno, M.; Takaya, H.; Komiya, S.; Mizuho, Y.; Oyasato, N.; Hiraoka, M.; Hirano, M.; Fukuoka, A. *J. Am. Chem. Soc.* **1995**, *117*, 12436. (b) Gomez-Bengoa, E.; Cuerva, J. M.; Mateo, C.; Echavarren, A. M. *J. Am. Chem. Soc.* **1996**, *118*, 8553 and references therein.