Protonation of an η^6-Arene−Metal Complex To Yield a Metal−Hydrogen Bond via an Electrophilic Aromatic Substitution Mechanism

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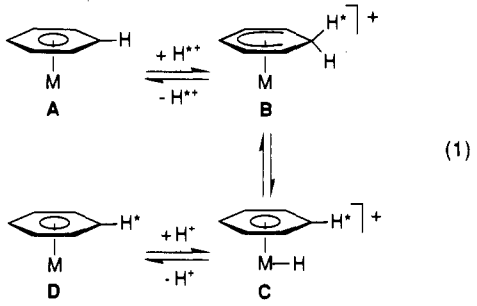
Alternative mechanistic pathways have been envisioned for electrophilic exchange of the protons of arene ligands.[1] One pathway involves direct addition of the proton to the less-hindered *exo* face of the arene ligand to give an arenium ion complex, which then loses a proton, perhaps via a metal−hydride intermediate,[2] to give the product (eq 1, **A** → **B** → **C** → **D**). Another pathway involves protonation of the metal to give a metal−hydride, which then rearranges to a similar arenium ion complex and eventually the product (eq 1, **D** → **C** → **B** → **A**).[3] The key to distinguishing between these two



mechanistic pathways is interception of the intermediates.[4] We are intrigued by compounds that have the general formula (arene)ML_3, where M is a group 6 metal and L is a carbonyl or phosphine ligand. Such compounds are known to undergo acid-induced isotopic substitution of the arene hydrogen atoms,[5] and they can be protonated at the metal to give metal hydrides.[6,7] We demonstrate in the present study that protonation of (η^6-C_6H_6)Mo(TRIPOD),[8] **1**, to give the metal−hydride complex [(η^6-C_6H_6)Mo(TRIPOD)H]$^+$, **3**, takes place via *exo* addition of a proton to the arene ligand followed by migration to the metal of the *endo* proton of the resulting arenium ion complex[9] [(η^5-C_6H_7)Mo(TRIPOD)]$^+$, **2** (Figure 1, **1** → **2b** → **3b**; cf. eq 1, **A** → **B** → **C**).[10]

The new complex **1** was synthesized in a melt reaction containing (η^6-C_6H_6)$_2$Mo and TRIPOD.[11] Green *et al.* have previously shown that related complexes that bear monodentate phosphine ligands can be protonated at the metal to give metal−hydride complexes.[6] Compound **1** is protonated upon addition of one equiv of H^+ to yield the red crystalline product **3**.[12] The protonated complex **3** exhibits dynamic ^1H, ^{13}C, and ^{31}P NMR spectra and apparent C_3 symmetry until the sample is cooled, whereupon decoalescence occurs and the C_s symmetry of the compound is revealed.[13] The hydride ligand apparently does not lie along the axis of the parent compound **1** (in the pocket of the TRIPOD ligand), but in an equatorial position between two of the phosphine atoms.[14] This geometry was confirmed when the solid-state structure of **3**·(PF_6) was determined (Figure 2).[15] The hydride ligand was located in the final difference map as the largest peak. The location of the hydride ligand is also indicated by the observed distortion of the metal's coordination sphere.

Treatment of **1** with 1 equiv of trifluoromethanesulfonic acid-d_1 in dichloromethane gave **3b** (Figure 1). Compound **3b** was characterized by ^1H and ^{31}P NMR spectroscopy and, after deprotonation with NaOMe, by DIP and FAB MS. The NMR data reveals the presence of a Mo−H (not a Mo−D) bond. The parent peaks of the deprotonated product **1**-d_1 were 1 *m/z* unit

(1) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkins, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 1016−1026.

(2) We are unaware of a precedent in the literature for such a metal−hydride intermediate forming after electrophilic attack on an arene, but it is the mechanism that will be proposed herein. Protonation and Friedel−Crafts acetylation reactions of ferrocenes are believed to proceed via a similar mechanism, but the metal−hydride products are not isolated: (a) Cunningham, A. F., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 4864. (b) McKee, M. L. *J. Am. Chem. Soc.* **1993**, *115*, 2818. (c) Mueller-Westerhoff, U. T.; Haas, T. J.; Swiegers, G. F.; Leipert, T. K. *J. Organomet. Chem.* **1994**, *472*, 229.

(3) This is the mechanism that has been previously suggested for the electrophilic aromatic substitution of (arene)CrL_3 (L = CO, PR_3) compounds: (a) Sneeden, R. P. A. *Organochromium Compounds*; Academic Press: New York, 1975; pp 195−197. (b) Setkina, V. N.; Baranetskaya, N. K.; Ginzburg, A. G.; Zdanovich, V. I.; Nefedova, M. N.; Kursanov, D. N. *J. Organomet. Chem.* **1973**, *61*, 287.

(4) These two pathways are the reverse of one another. The principle of microscopic reversibility dictates that under equilibrium conditions both mechanisms would be operative.

(5) Tsoy, A. A.; Baranetskaya, Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1981**, *212*, 377. See also ref 3 and references therein.

(6) (a) Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *J. Chem. Soc. A* **1971**, 2929. (b) Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1361.

(7) The studies of protonation of (arene)M(PR_3)$_3$ systems follow the earlier studies of the protonation of (arene)M(CO)$_3$ complexes, first described by Wilkinson, *et al.*: Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

(8) TRIPOD = 1,1,1-tris[(diphenylphosphino)methyl]ethane.

(9) This study does not distinguish between a relatively stable intermediate arenium ion complex and a concerted transfer of the proton to and from the arene ligand.

(10) A related mechanism was proposed for the acid-induced cleavage of a C-P bond to convert an η^6-arylphosphine to an η^6-benzene ligand, but it was ruled out in a crossover experiment: Morris, R. H.; Sawyer, J. F.; Schweitzer, C. T.; Sella, A. *Organometallics* **1989**, *8*, 2099 (see Scheme IV).

(11) For **1**: Mo(C_6H_6)$_2$ (0.34 g, 1.35 mmol) and TRIPOD (0.76 g, 1.22 mmol) were heated in a sealed glass tube under vacuum at 160 °C for 2 days. The tube was opened under nitrogen, the contents were extracted with 1:1 benzene/heptane (~30 mL), and the extract was filtered. The red-orange product crystallized from the solvent upon cooling to 5 °C (0.62 g, 64%). ^1H NMR (C_6D_6, 500 MHz): δ 1.16 (m, 3 H, CH_3), 2.17 (m, 6 H, CH_2), 4.41 (m, 6 H, C_6D_6), 6.85 (t, J = 7 Hz, 12 H, Ph), 6.96 (t, J = 7 Hz, 6 H, Ph), 7.08 (m, 12 H, Ph). $^{31}P\{^1H\}$NMR (C_6D_6, 202 MHz): δ 46.59 (s). Anal. Calcd (found) for $C_{47}H_{45}P_3Mo$ (798.74): C, 70.68 (70.44), H, 5.68 (5.74).

(12) For **3**·(PF_6): All operations were carried out under an Ar atmosphere. **1** (0.37 g, 0.46 mmol) was dissolved in CH_2Cl_2 (10 mL), and HPF_6 (60% in water, 0.5 mL) was added. After being stirred for 15 min, the solution was extracted with water (2 × 10 mL) and then dried over $CaCl_2$. Evaporation yielded a red solid, which was recrystallized from CH_2Cl_2/Et_2O (0.24 g, 56%). ^1H NMR ($CDCl_2F$, −125 °C, 500 MHz): δ −6.36 (td, $J_{P_{trans}-H}$ = 16 Hz, $J_{P_{cis}-H}$ = 62 Hz, 1 H, Mo−H), 1.54 (br s, 3 H, CH_3), 2.19, 2.65 (br m, 4 H, diastereotopic CH_2), 2.31 (br s, 2H, CH_2), 5.30 (s, 6 H, C_6H_6), 6.63 (m, 4 H, Ph), 6.90 (m, 4 H, Ph), 7.01 (m, 8 H, Ph), 7.12 (m, 6 H, Ph), 7.20 (m, 4 H Ph), 7.28 (m, 4 H, Ph). $^{31}P\{^1H\}$NMR ($CDCl_2F$, −125 °C, 202 MHz): δ 34.52 (t, 1 P, J_{PP} = 62 Hz), 43.23 (d, 2 P). Anal. Calcd (found) for $C_{47}H_{46}P_4F_6Mo$ (944.71): C, 59.76 (59.48), H, 4.91 (4.95).

(13) For an EHMO investigation of the protonation of (arene)M(CO)$_3$ (M = Cr, W) and the dynamic behavior of the resulting metal−hydride complex, see: Mailvaganam, B.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1990**, *9*, 1089. For a NMR study of the stereochemical nonrigidity of (arene)M(CO)$_2$(PR_3)H complexes, see: Flood, T. C.; Rosenberg, E.; Sarhangi, A. *J. Am. Chem. Soc.* **1977**, *99*, 4334.

(14) For the structures of related (arene)ML_3H complexes, see: (a) Thi, N. P. D.; Spichiger, S.; Paglia, P.; Bernardinelli, G.; Kündig, E. P. *Helv. Chim. Acta* **1992**, *75*, 2593. (b) Green, M. L. H.; Hughes, A. K.; Lincoln, P.; Martin-Polo, J. J.; Mountford, P.; Sella, A.; Wong, L.; Bandy, J. A.; Banks, T. W.; Prout, K.; Watkin, D. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2063. (c) Reference 10.

(15) Crystal data for **1**: $C_{47}H_{45}P_3Mo$ (798.73), monoclinic, $P2_1/n$ (No. 14), T = −70 °C, a = 9.636(4) Å, b = 20.277(5) Å, c = 19.670(3) Å, β = 93.05(2)°, V = 3838(2) Å^3, Z = 4, 505 parameters, 6751 unique reflections, 5242 reflections with $I > 2\sigma(I)$, R = 0.042, R_w = 0.052. Crystal data for **3**·(PF_6): $C_{47}H_{46}F_6P_4Mo$ (944.71), monoclinic, $P2_1/n$ (No. 14), T = −100 °C, a = 22.944(2) Å, b = 10.071(2) Å, c = 18.184(2) Å, β = 102.660(8)°, V = 4100(1) Å^3, Z = 4, 562 parameters, 7183 unique reflections, 5486 reflections with $I > 2\sigma(I)$, R = 0.033, R_w = 0.037. A face-indexed numerical absorption correction was carried out for **3**·(PF_6).

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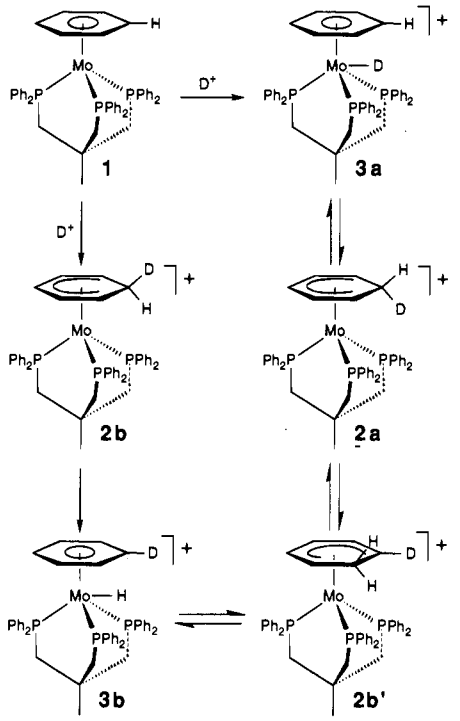

Figure 1. Kinetic products possible upon addition of D^+ to (η^6-C_6H_6)-Mo(TRIPOD) via (i) direct attack on the metal (**1** → **3a**) and (ii) indirect attack via an arenium ion complex (**1** → **2b** → **3b**). The equilibria (**3a** ⇌ **2a** ⇌ **2b′** ⇌ **3b**) could explain the incorporation of deuterium into the arene ligand even if the initial protonation is at the metal (**1** → **3a**), but selective spin inversion transfer (SSIT) NMR studies rule out such equilibria (see text). Only one arene hydrogen atom is shown for the sake of clarity.

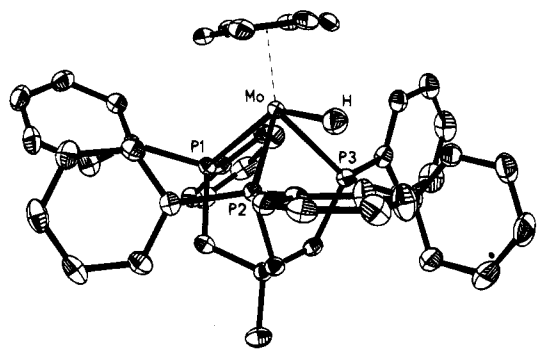

Figure 2. The structure of [(η^6-C_6H_6)Mo(TRIPOD)H]$^+$, **3**·(PF_6). Atoms are represented by thermal vibration ellipsoids at the 50% level. Hydrogen atoms (except for the hydride ligand) have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mo−P1 = 2.5127(9), Mo−P2 = 2.4298(10), Mo−P3 = 2.4568(9), Mo−H = 1.66(4), P1−Mo−P2 = 83.03(3), P1−Mo−P3 = 81.29(3), P2−Mo−P3 = 87.41(3), P1−Mo−H = 139.6(12), P2−Mo−H = 68.7(13), P3−Mo−H = 69.6(12). There is no significant contact between the counteranion and the hydride ligand.

higher than those of the undeuterated compound.[16] The latter experiment suggests that the arene ligand is involved in the protonation of the metal center, but it does not demonstrate that the hydride ligand originates from the arene, for it could originate from another source of protium, e.g., from the solvent. In a complementary experiment, the perdeuterioarene derivative **1**-d_6, which was synthesized from (η^6-C_6D_6)$_2$Mo, was treated with 1 equiv of trifluoromethanesulfonic acid-d_0 in dichloromethane to yield [(η^6-C_6D_5H)Mo(TRIPOD)D]$^+$, **3c**. Compound **3c** was characterized by ^{1}H and ^{31}P NMR spectroscopy and, after deprotonation with NaOMe to give **1**-d_5, by DIP and FAB MS. The protonation experiment employing **1**-d_6 demonstrates that the hydride ligand originates from the arene ligand.

While the origin of the hydride ligand is demonstrated by the tracer studies, these experiments do not unambiguously demonstrate that the initial attack is *exo* (**1** → **2b** → **3b**). If the hydride ligand exchanges rapidly with the hydrogens of the arene ligand (**3a** ⇌ **2a** ⇌ **2b′** ⇌ **3b**) and one ignores isotope effects, statistics dictate a 1:6 ratio of **3a**:**3b**. Thus, the initial intermolecular attack could be at the metal (**1** → **3a**), followed by intramolecular *endo* protonation of the arene (**3a** → **2a**), a hydrogen shift (**2a** → **2b′**), and finally transfer of the *endo* proton to the metal (**2b′** → **3b**). However, it is possible to differentiate these two pathways experimentally; we have qualitative kinetic information that rules out the **1** → **3a** → **2a** → **2b′** → **3b** pathway. We have prepared equimolar solutions of **1** and trifluoromethanesulfonic acid-d_1 at −150 °C in $CDCl_2F$ and found protonation does not occur until the solution is warmed to ca. −85 °C.[17] The first product that is observed in these experiments is **3b**. Selective spin inversion transfer (SSIT) NMR experiments at 25 °C indicate that no spin exchange takes place between the arene ligand hydrogens and the metal hydride on the time scale of nuclear relaxation ($T_1 \approx 1$ s).[18] Extrapolating to −85 °C, the rate of formation of **3b** must be much faster than the rate of intramolecular chemical exchange (**3a** ⇌ **2a** ⇌ **2b′** ⇌ **3b**).

We conclude from these experiments that **1** is protonated at the metal to give the metal−hydride complex **3** via a mechanism that involves initial protontation of the arene ligand to give an arenium ion complex (Figure 1, **1** → **2b** → **3b**).[19] To our knowledge, these data provide the first experimental evidence of electrophilic substitution of an arene ligand via an *exo* mechanism.

Acknowledgment. This work was made possible by the Oklahoma Center for the Advancement of Science and Technology award for Project No. HN3-007. We thank Prof. T. E. Bitterwolf for bringing ref 2c to our attention and Prof. B. M. Fung for his assistance with the SSIT NMR pulse sequence.

Supporting Information Available: Tables of the crystallographic data of **1** and **3**·(PF_6) and representative spectra (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) The fact that only **1**-d_1 was obtained demonstrates that deprotonation of **3b** by NaOMe, a strong base, is not the microscopic reverse of protonation of **1** by strong acids.

(17) It has been noted that CF_3SO_3H freezes very rapidly in CH_2Cl_2 at −95 °C and is not dissolved: Rothfuss, H.; Gusev, D. G.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 2894. The protonation of **1** is probably very fast at low temperature, and warming to −85 °C is necessary to dissolve the acid.

(18) Because of the large difference in frequency between the arene and hydride resonances, the standard spin inversion transfer (SIT) pulse sequence was impractical. An alternative pulse sequence was devised. Selective spin inversion transfer (SSIT) data were collected with a Varian VXR-500 NMR using the two-pulse sequence d_1, $2\pi/2$, τ_m, $\pi/2$, aq. The transmitter offset frequency was centered on the arene resonance. The relaxation delay d_1 was set equal to 5 times the longest T_1 to allow complete longitudinal relaxation between pulses. The 180° pulse was of sufficiently low power (and long duration) that surrounding resonances were unaffected. The mixing time τ_m was varied between 0.001 s and $5T_1$. A 90° pulse was applied at full power prior to FID acquisition. Data analysis for the SSIT pulse sequence is the same as for the SIT pulse sequence: Ashby, M. T.; Govindan, G. N.; Grafton, A. K. *J. Am. Chem. Soc.* **1994**, *116*, 4801.

(19) Protonation is probably not orbital controlled (cf.: Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441) since the frontier orbitals of (arene)MoL_3 compounds are metal-based orbitals (Mo d_{xy}, Mo $d_{x^2-y^2}$, Mo d_{z^2}) that do not mix substantially with the orbitals of the arene ligand: (a) Modelli, A.; Distefano, G.; Guerra, M.; Jones, D. *J. Am. Chem. Soc.* **1987**, *109*, 4440. (b) See also the discussion and personal communication cited in ref 14b.