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PROTONATION OF METAL–METAL BONDS IN HETEROBIMETALLIC COMPOUNDS LINKED BY A HETERODIFUNCTIONAL LIGAND

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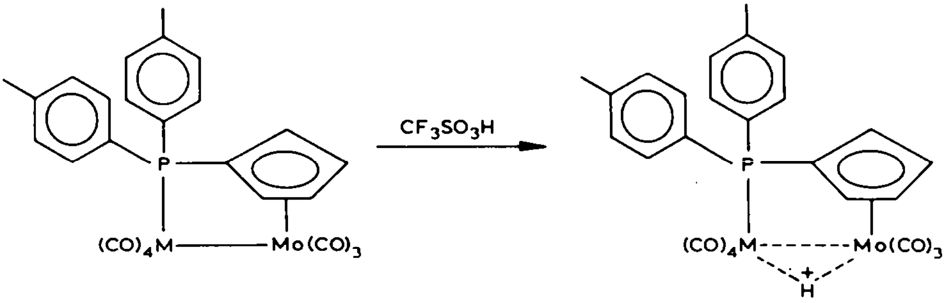
Summary

Addition of trifluoromethanesulfonic acid to the heterobimetallic compounds $(CO)_4\overline{ReMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}p\text{-}CH_3)_2]$ (I) and $(CO)_4\overline{MnMo(CO)_3[\eta^5\text{-}C_5H_4P}(C_6H_4\text{-}p\text{-}CH_3)_2]$ (II) results in protonation of the metal–metal bond to give cationic compounds with bridging hydrides (III and IV). Deprotonation of III and IV with triethylamine regenerates I and II in high yield.

Cationic mononuclear metal hydrides such as $(C_5H_5)_2ReH_2^+$ [1] and $(C_5H_5)_2WH_3^+$ [2] can be prepared by protonation of the neutral hydrides $(C_5H_5)_2ReH$ and $(C_5H_5)_2WH_2$. Bimetallic metal–metal bonded complexes such as $[(C_5H_5)Mo(CO)_3]_2$ and $[(C_5H_5)Fe(CO)_2]$ react with 98% sulfuric acid to give protonation of the metal–metal bond [3]. More recent studies by Gray [4], Cutler [5], Poilblanc [6] and others [7] provide additional information about the formation and reactivity of bimetallic compounds with protonated metal–metal bonds. We report



(I, M = Re;
II, M = Mn)

(III, M = Re;
IV, M = Mn)

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that the Re–Mo and Mn–Mo bonds of I and II are protonated by trifluoromethanesulfonic acid to give cationic monohydrides III and IV.

Results

Earlier we synthesized the heterobimetallic Mo–Re (I) and Mo–Mn (II) compounds as possible precursors of heterobimetallic dihydrides that might serve as reducing agents. However, reaction of I and II with > 1000 psi H_2 failed to produce any metal hydride species up to their decomposition temperatures (120°C for I, 170°C for II). We therefore investigated the possibility of converting I and II into metal dihydrides by sequential treatment with acid and then a hydride donor.

The addition of CF_3SO_3H (2.5 μl, 1.5 equiv) to a 67 mM CD_2Cl_2 solution of I caused an immediate color change from yellow to light orange and resulted in the appearance of a singlet at -16.87 ppm characteristic of a bridging metal hydride. The appearance of this peak was accompanied by the disappearance of all resonances due to I and their replacement by new peaks due to III. The pseudo-quartets (peak splitting ≈ 2 Hz) at δ 4.61 and 5.51 for the two pairs of cyclopentadienyl protons on I were replaced by broad singlets at δ 5.37 and 6.08. The shift of these resonances to lower field is consistent with the formation of cationic product III.

The ^{13}C NMR carbonyl resonances of the protonated Re–Mo compound III were shifted upfield 4–13 ppm from their positions in I. The molybdenum carbonyls of III gave rise to two singlets in a 1/2 intensity ratio, and the rhenium carbonyls gave rise to three phosphorus coupled doublets in a 2/1/1 ratio. The cyclopentadienyl carbons also underwent significant changes when I was protonated. The three doublets for the cyclopentadienyl carbons of I at δ 89.7, 89.2, and 61.6 were replaced by three new doublets at 95.4, 94.1 and 84.4. It is interesting to note that the cyclopentadienyl carbon bonded to phosphorous appears only ~ 10 ppm upfield of the other two cyclopentadienyl carbons in III, but in I this carbon's resonance is separated from the other two cyclopentadienyl resonances by ~ 27 ppm. This may reflect a relief of strain in the ring upon protonation of I.

Protonation of I to form III causes the metal carbonyl stretches to move to higher energy. In CH_2Cl_2 solution, the IR bands of I appear at 2082m, 1988s, 1963s, 1936m, 1896m, and 1867m cm^{-1}. III has bands at 2119m, 2064m, 2040sh, 2027s and 1995m, br cm^{-1}.

III is easily deprotonated to regenerate I. In an NMR experiment, a 67 mM solution of III prepared by adding 2.5 μl CF_3SO_3H to 14.5 mg I in 0.29 ml CD_2Cl_2 is cleanly and completely deprotonated by 60 μl of $(CD_3)_2CO$. In a larger scale experiment, I was protonated, deprotonated, and recovered in almost quantitative yield. Thus, addition of 100 μl CF_3SO_3H to 221.3 mg I in 8 ml CH_2Cl_2 resulted in complete conversion to III as observed by IR. Addition of 0.60 ml NEt_3 caused the orange color of III to revert back to the yellow color of I. Evaporation of the solvent and chromatography of the residue (silica gel, Et_2O) gave 218.0 mg I (98%).

In an analogous manner, the Mn–Mo bond of II was protonated to give IV, which exhibited a doublet (J(PH) 6.2 Hz) at -19.21 ppm for the bridging metal hydride. As in the case of I, protonation of II caused the ^{13}C NMR resonance of the cyclopentadienyl carbon bonded to phosphorous to move downfield by more than 20 ppm; the doublet at δ 57.3 (J(PC) 50.5 Hz) in II is replaced by a doublet at 78.6 (J(PC) 41.3 Hz) in IV. Other changes in the ^1H NMR, ^{13}C NMR and IR were similar to the changes observed for the I → III conversion. The protonation, deprotonation and re-isolation of pure II was also carried out with > 90% recovery of II.

In an effort to determine whether weaker acids could be used to protonate I or II, trifluoroacetic acid was added to CH_2Cl_2 solutions of I and II. A 26 m*M* solution of I prepared by dissolving 40.0 mg I in 2 ml CH_2Cl_2 was shown by IR to be partially protonated after addition of 0.21 ml CF_3CO_2H (1.2 *M*). An additional 0.20 ml CF_2CO_2H (2.2 *M*) caused complete protonation of I. Similarly, a 26 m*M* solution of II prepared by dissolving 32.5 mg of II in 2 ml CH_2Cl_2 was partially protonated by addition of 0.20 ml CF_3CO_2H (1.2 *M*); an additional 0.80 ml CF_3CO_2H (4.3 *M*) caused complete conversion to IV.

A competition experiment was performed to qualitatively determine the relative basicity of I and II. When a CD_2Cl_2 solution containing 2.4×10^{-5} mol of I and 2.4×10^{-5} mol of II was treated with 3 μl CF_3SO_3H, the hydride resonance of III was observed at δ − 16.9 but no hydride resonance of IV was observable at δ − 19.2. This indicates that the basicity of the Re–Mo bond of I is greater than the basicity of the Mn–Mo bond of II.

In an attempt to covert protonated compounds III and IV into heterobimetallic dihydrides, we investigated their reactions with Li^+ $HB(CH_2CH_3)_3^-$. However, no dihydrides are observed and the cations were simply deprotonated to regenerate I and II in good yield.

Discussion

The very large upfield chemical shifts of III and IV indicate that the hydride is bridging rather than terminal [8]. Early X-ray diffraction results [9] were taken as evidence for a linearly protonated metal–metal bond in $[Cr_2(CO)_{10}(\mu_2\text{-}H)]^-[NEt_4]^+$, but it was later shown by neutron diffraction [10] that the Cr–H–Cr angle is 158.9(6)°. Other compounds containing three-center two-electron M–H–M bonds have also been shown by neutron diffraction to have non-linear M–H–M bonds; $W_2(\mu_2\text{-}H)(CO)_9(NO)$ has a W–H–W angle of 125.0(2)° [11] and $Mo_2(C_5H_5)_2(CO)_4(\mu_2\text{-}H)(\mu_2\text{-}PMe_2)$ has a Mo–H–Mo angle of 122.9 (2)° [12]. The bonding in the cationic hydrides III and IV is thus probably best represented as a three-center two-electron bond with the hydrogen atom displaced from the metal–metal axis.

Experimental

General. All reactions were conducted under an atmosphere of dry nitrogen. CH_2Cl_2 was distilled under N_2 from CaH_2 prior to use. ^1H NMR spectra were recorded on a Bruker WH-270 (270 MHz); ^{13}C NMR spectra were recorded on a JEOL FX-200 (50.1 MHz). Infrared spectra were recorded on either a Beckman 4230 infrared spectrometer or a Digilab FTS-20 interferometer. I and II were prepared as reported earlier [13].

Protonation of I

I (14.5 mg, 1.92×10^{-5} mol) was dissolved in CD_2Cl_2 (0.29 ml) and treated with CF_3SO_3H (0.8 μl, 0.5 equiv). Integration of the NMR resonances indicated about equal amounts of I and III. An additional 1.7 μl CF_3SO_3H resulted in complete conversion to III. ^{1}H NMR (CD_2Cl_2): δ -16.87 (d, 1H, Mo–H–Re), 2.42 (s, CH_3), 5.37 (br, s, 2H, C_5H_4P), 6.08 (br, s, 2H, C_5H_4P), 7.43 (dd, J(HH) 7.9 Hz, J(PH) 2.3 Hz, *meta*), 7.72 (dd, J(PH) 13.2 Hz, J(HH) 8.2 Hz, *ortho*). ^{13}C NMR (CD_2Cl_2): δ 21.6 (s, CH_3), 84.4 (d, J(PC) 47.4 Hz, C(1) of C_5H_4P), 94.1 (d, J(PC) 9.2 Hz, C(2) of C_5H_4P), 95.4 (d, J(PC) 6.1 Hz, C(3) of C_5H_4P), 120.2 (q, J(CF) 320.0 Hz, CF_3), 124.9 (d, J(PC) 55.1 Hz, *ipso*), 131.6 (d, J(PC) 12.2 Hz, *meta*), 132.8 (d, J(PC) 13.8 Hz, *ortho*), 145.5 (s, *para*), 178.9 (d, J(PC) 39.7 Hz, Re(CO) *trans* to P), 180.2 (d, J(PC) 7.6 Hz, Re (CO) *trans* to Mo), 180.8 (d, J(PC) 9.2 Hz, Re $(CO)_2$, carbonyls *trans* to each other), 220.0 (s, $Mo(CO)_2$), 225.7 (d, Mo(CO)).

Protonation of II

II (27.9 mg, 4.47×10^{-5} mol) was dissolved in CD_2Cl_2 (0.21 ml) and treated with CF_3SO_3H (8 μl, 2 equiv). The orange color of II darkened slightly, and the NMR spectrum indicated complete conversion to IV. To obtain sharp lines in the NMR spectra, it was necessary to centrifuge the NMR tubes to remove traces of solids. ^{1}H NMR (CD_2Cl_2): δ -19.21 (d, J(PH) 6.2 Hz, 1H, hydride), 2.42 (s, CH_3), 5.32 (s, 2H, C_5H_4P), 6.02 (s, 2H, C_5H_4P), 7.46 (d, J(HH) 6.2 Hz, *meta*), 7.78 (dd, J(PH) 14.0 Hz, J(HH) 7.9 Hz, *ortho*); ^{13}C NMR (CD_2Cl_2): δ 21.6 (s, CH_3), 78.6 (d, J(PC) 41.3 Hz, C(1) of C_5H_4P), 93.4 (d, J(PC) 9.2 Hz, C(2) of C_5H_4P), 94.9 (d, J(PC) 4.6 Hz, C(3) of C_5H_4P), 119.5 (q, J(CF) 316.6 Hz, CF_3), 126.4 (d, J(PC) 50.5 Hz, *ipso*), 131.8 (d, J(PC) 12.2 Hz, *meta*), 132.4 (d, J(PC) 12.2 Hz, *ortho*), 145.8 (s, *para*), 207 (br, s, $Mn(CO)_4$), 219.6 (s, $Mo(CO)_2$), 225.5 (s, Mo(CO)); IR (CH_2Cl_2): 2106m, 2062m, 2040sh, 2029s, 1999m, 1978m cm^{-1}.

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