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Oxidation and Acidolysis of $MoH_4(PR_3)_4$

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$MoH_4(PMe_2Ph)_4$ reacts with 2 mol of $AgBF_4$ in MeCN to give $[MoH_2(PMe_2Ph)_4(NCMe)_2](BF_4)_2$, characterized by spectroscopic methods and X-ray crystallography as containing a fluxional dodecahedral dication. Reaction with equimolar $AgBF_4$ gives no new product but only a reduced yield of the same salt. This oxidation is thus followed by reductive elimination of H_2 so that the molybdenum oxidation state suffers no net change. The same salt is obtained by treating the tetrahydride with 2 mol of $HBF_4{\cdot}OEt_2$ in acetonitrile. The identity of the phosphine affects the product isolated: $MoH_2(PMePh_2)_4$, upon treatment with $AgBF_4$ or $HBF_4{\cdot}OEt_2$ in MeCN, yields $MoH_2(PMePh_2)_3(NCMe)_3^{2+}$ with liberation of 1 mol of $PMePh_2$. Possible mechanisms are discussed, as is the relationship between silver oxidation and acidolysis. Crystallographic data (at −160 °C) for $[MoH_2(PMe_2Ph)_4(NCMe)_2](BF_4)_2$: monoclinic space group $P2_1$ with $a = 12.359$ (6) Å, $b = 33.323$ (2) Å, $c = 13.048$ (6) Å, $\beta = 128.61$ (2)°, $Z = 4$. $R(F) = 0.0673$ for 5037 data collected by diffractometer.

Introduction

The reactivity patterns of 16- and 18-electron complexes are becoming increasingly well catalogued and, in some cases, understood.[1] Workers pursuing the topic of the reductive oligomerization of CO (e.g., Fischer–Tropsch chemistry), as either a stoichiometric or catalytic reaction, are experiencing considerable difficulty in achieving such goals within the confines of 16/18 electron reactivity patterns.[2-8] This is related in part to the observation that the following CO reduction equilibrium generally favors reactants, independent of whether n equals 0 or 1.

$$L_mHMCO + nL' \rightleftharpoons L_mL'_nMCHO \tag{1}$$

We have initiated a project designed to explore the possibility that CO hydrogenation will occur with lower activation energy when carried out on paramagnetic (i.e., odd-electron) metal centers.[9-12] One way in which this might occur is by an improvement in the thermodynamics (and activation energy) of eq 1. As a preliminary to any reactions with CO, we chose to attempt the production of a 17-electron hydride complex by a chemical 1-electron oxidation. The oxidant selected was $AgBF_4$, chosen because Ag^0 can be separated easily from the hydride product and also because it contains a "nearly" noncoordinating counterion. The type of hydride chosen, $MoH_4(PR_3)_4$, continues our interest in high-valent transition-metal hydrides[13] but is anticipated to be susceptible to oxidation due to its heavy complement of electron-donating phosphine ligands. We therefore set out to produce and establish the reactivity of $MoH_4(PR_3)_4{}^{+\cdot}$.

Experimental Section

General Procedures. All operations were carried out under prepurified nitrogen with solvents dried and deoxygenated by using conventional procedures. Molybdenum pentachloride and $HBF_4{\cdot}Et_2O$ were commercial products and were used as received. The latter is a liquid, which was used neat. IR spectra were recorded on a Perkin-Elmer 283 spectrometer and calibrated by using polystyrene film. Proton NMR spectra were recorded on a Varian HR-220 spectrometer, while ^{31}P NMR spectra were recorded on a Varian XL-100 spectrometer. All chemical shifts are reported on the δ scale, with ^{31}P shifts downfield of the reference (85% H_3PO_4) being positive. The "hydride-coupled" ^{31}P NMR spectra (i.e., selective decoupling of only protons downfield of Me_4Si) always suffer some partial transfer of decoupler power into the hydride protons. This has the consequence that the observed line spacing is smaller than the actual $^2J_{H-Mo-P}$ value. This must be borne in mind when the reported *apparent J* values (derived from ^{31}P NMR spectra) are considered. The line multiplicity remains a reliable guide for counting protons, however.

$MoH_4(PMe_2Ph)_4$.[14] A mixture of 5.0 g (11.9 mmol) of $MoCl_3(THF)_3$,[15] 10 cm^3 (70 mmol) of PMe_2Ph, and 3.8 g (158 mmol) of amalgamated Mg powder in 100 mL of THF was stirred *vigorously* under 100 atm of H_2 for 20 h. The yellow-brown THF solution was filtered through a coarse frit, stripped of solvent, extracted with toluene, and filtered again to give a toluene solution of $MoH_4(PMe_2Ph)_4$. This was evaporated to ~25 mL and precipitated by the addition of an excess of MeOH at −78 °C.

Caution should be exercised when precipitating $MoH_4(PMe_2Ph)_4$ from toluene with MeOH as, at room temperature, MeOH decomposes $MoH_4(PMe_2Ph)_4$ within 1–2 h. All manipulations should be done at −78 °C.

Alternatively, comparable yields can be obtained by crystallizing yellow needles of $MoH_4(PMe_2Ph)_4$ from toluene with an equal volume amount of CH_3CN after cooling to −20 °C overnight. The needles should be filtered at −20 °C with a coarse frit. The product is a yellow solid. Yield: 3.6 g (46% based on $MoCl_3(THF)_3$).

Silver(I) Oxidation of $MoH_4(PMe_2Ph)_4$. Solid silver tetrafluoroborate (0.317 g, 1.63 mmol) was added to a slurry of $MoH_4(PMe_2Ph)_4$ (0.53 g, 0.81 mmol) in CH_3CN (30 mL). The yellow slurry turned a yellow-green with concomitant evolution of H_2 and deposition of black silver metal. The solution was filtered to give a gold-yellow filtrate, which was concentrated under vacuum. Subsequent addition of ~40 mL of toluene and cooling to −20 °C overnight gave yellow crystals (0.48 g, 65% yield) of $[MoH_2(PMe_2Ph)_4(CH_3CN)_2](BF_4)_2$. IR (KBr, cm^{-1}): $\nu_{C\equiv N}$, 2310 (w) and 2275 (w); ν_{B-F}, 1050 (s, br). ^1H NMR (CD_3CN): δ 7.52 and 7.24 (multiplets, intensity 10), 1.40 (virtual triplet, intensity 6), 1.68 (virtual triplet, intensity 6), −3.60 (triplet of triplets, $J_{P_A-H} = 35$ Hz, $J_{P_B-H} = 65$ Hz, intensity 1). $^{31}P\{^1H\}$ NMR (CD_3CN): δ +20.62 (t, $J = 17$ Hz), 1.97 (t, $J = 17$ Hz). ^{31}P\{hydride coupled\} (CD_3CN): δ 20.6 (septet, spacing 21 Hz), 2.00 (quintet, spacing 22 Hz).

Acidolysis of $MoH_4(PMe_2Ph)_4$. A slight excess of 2 mol of $HBF_4{\cdot}Et_2O$ was added to a CD_3CN slurry of $MoH_4(PMe_2Ph)_4$ in an NMR tube. The yellow slurry evolved hydrogen and dissolved to yield a yellow solution. The resulting ^1H and ^{31}P NMR spectra were identical with those of $[MoH_2(PMe_2Ph)_4(CH_3CN)_2](BF_4)_2$ prepared by silver oxidation.

Ligand Substitution of $[MoH_2(PMe_2Ph)_4(CH_3CN)_2](BF_4)_2$. Refluxing $[MoH_2(PMe_2Ph)_4(CH_3CN)_2](BF_4)_2$ in CH_3CN for 30 min

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Table I. Crystal Data for $[MoH_2(PMe_2Ph)_4(NCMe)_2](BF_4)_2$

empirical formula	$C_{36}H_{52}N_2B_2F_8P_4Mo$
color	greenish yellow
cryst dimens	0.16 × 0.20 × 0.24 mm
space group	$P2_1$
cell dimens (at −160 °C; 52 reflcns)	
a	12.359 (6) Å
b	33.323 (21) Å
c	13.048 (6) Å
β	128.61 (2)°
molecules/cell	4
cell vol	4198.58 Å^3
calcd *d*	1.43 g/cm^3
wavelength	0.710 69 Å
mol wt	906.3
linear abs coeff	5.2 cm^{-1}
no. of unique intens	5619
no. with $F > 0.0$	5393
no. with $F > \sigma(F)$	5235
no. with $F > 2.33\sigma(F)$	5037
final residuals	
$R(F)$	0.0673
$R_w(F)$	0.0667
goodness of fit for the last cycle	1.434
max Δ/σ for last cycle	0.05

yielded a brown solution, which gave ^1H and ^{31}P NMR spectra consistent with replacement of one coordinated PMe_2Ph by CH_3CN. The new compound is formulated as $[MoH_2(PMe_2Ph)_3(CH_3CN)_3](BF_4)_2$. ^1H NMR (CD_3CN): δ 7.45 (multiplet), −3.85 (quartet, J = 57.5 Hz), +1.28 (doublet, J = 3 Hz, due to free PMe_2Ph), +1.69 ("filled-in" doublet, J = 9 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 26.5 (singlet), −45.8 (singlet, due to free PMe_2Ph). ^{31}P\{hydride coupled\} (CD_3CN): δ 26.4 (triplet, spacing 38 Hz), −45.8 (singlet).

Silver(I) Oxidation of $MoH_4(PMePh_2)_4$. Solid silver tetrafluoroborate (0.01 g, 0.04 mmol) was added to a CH_3CN (3 mL) slurry of $MoH_4(PMePh_2)_4$[16] (0.02 g, 0.02 mmol) at ambient temperature. The slurry became a yellow solution with concomitant evolution of H_2 and deposition of black silver metal. Filtering the solution gave a yellow solution. On the basis of the spectral data the formula of the compound is assigned $[MoH_2(PMePh_2)_3(CH_3CN)_3](BF_4)_2$. ^1H NMR (CD_3CN): δ 7.52 (m, 12 H), 7.41 (m, 18 H), −1.98 (quartet, J = 55 Hz), +1.89 (filled-in doublet). $^{31}P\{^1H\}$ NMR (CD_3CN): δ +41.3 (singlet). ^{31}P\{hydride coupled\} (CD_3CN): δ +41.2 (triplet, spacing 26 Hz).

Acidolysis of $MoH_4(PMePh_2)_4$. A slight excess of $HBF_4 \cdot Et_2O$ was added to a CH_3CN slurry of $MoH_4(PMePh_2)_4$ in an NMR tube. The slurry turned yellow and evolved hydrogen gas immediately upon addition of acid. The ^1H and ^{31}P NMR of this solution duplicated spectral data for the product of oxidation of $MoH_4(PMePh_2)_4$.

Crystallography. The crystal of $[MoH_2(PMe_2Ph)_4(NCMe)_2](BF_4)_2$ was grown by slow cooling of a MeCN/toluene solution of the salt to −20 °C. It was transferred to the goniostat and cooled to −160 °C for all subsequent measurements, by using our reported techniques.[17] Space group extinctions indicated either space group $P2_1$ or space group $P2_1/n$, the former being selected by intensity statistics and the successful solution obtained. Crystallographic data are presented in Table I. Intensity data (6° ≤ 2θ ≤ 45°) were not corrected for absorption. The structure was solved by using a combination of direct methods and Fourier summations. The asymmetric unit in this noncentrosymmetric space group contains two independent cations and four independent anions, for a total of 106 non-hydrogen atoms. Consequently, refinement (using the rejection criterion $F > 3\sigma(F)$) was carried out in a cyclic fashion, blocking independent ionic units; all non-hydrogen atoms except carbon were refined anisotropically. Hydrogen atoms were not located in this acentric space group. It was not possible to distinguish the absolute configuration of the particular crystal selected for data collection, due, perhaps in part, to the fact that the crystal contains equal amounts of near enantiomers. The final difference Fourier was essentially featureless, the largest peaks being found in the vicinity of the BF_4^- ions.

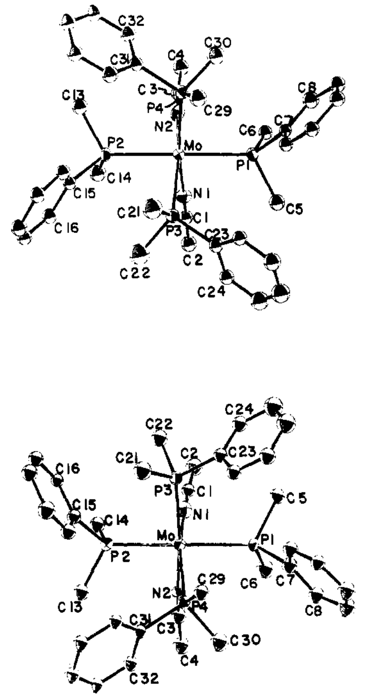

Figure 1. ORTEP views of $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$, showing two conformers found in the crystal: above, first conformer. The view is down an approximate C_2 axis of symmetry. No hydrogen atoms are shown.

The results of the crystallographic work are presented in Tables II–IV and Figures 1–3. Anisotropic thermal parameters (U_{ij} form) and observed and calculated structure factors are available as supplementary material.

Phenyl rings are all planar to within ±1σ; the C–C distances average 1.400 Å. The BF_4^- units are ordered with an average B–F distance of 1.376 Å and a F–B–F angle of 108.7°.

Results

The reaction of equimolar $MoH_4(PMe_2Ph)_4$ and $AgBF_4$ in CH_3CN at 25 °C occurs with gas evolution and yields a product, **1**, silver metal, and approximately 50% recoverable $MoH_4(PMe_2Ph)_4$. The use of a 2:1 ratio of Ag:Mo effects complete consumption of $MoH_4(PMe_2Ph)_4$ to give a quantitative yield (by ^1H and ^{31}P NMR) of the same product **1**. This product is a diamagnetic complex, the hydride ligand resonance of which is a triplet of triplets at 16 °C. Four phosphine ligands are indicated in **1**. When the temperature is lowered to −35 °C in CD_3CN, the hydride resonance shows selective broadening (i.e., two of the lines remain sharp) similar to that caused by intramolecular hydride scrambling in $MH_4(PR_3)_4$ (M = Mo, W). We have made no determined effort to record the limiting low-temperature spectrum. Consistent with the above evidence for two types of phosphine ligands, the phosphine methyl groups exhibit two chemical shifts at 16 °C, each resonance being a virtual triplet.

The number of hydride nuclei was determined by selective proton decoupling of the ^{31}P NMR spectrum. The completely proton-decoupled ^{31}P NMR spectrum of **1** is an A_2X_2 pattern at 35 °C ($^2J_{A-X}$ = 17 Hz). When only the methyl and phenyl protons are selectively decoupled, the downfield ^{31}P triplet becomes a seven-line multiplet, consistent with a triplet of triplets with $2J_{A-H} \approx J_{A-X}$. The upfield ^{31}P resonance in this hydride-coupled spectrum exhibits five lines, consistent with a triplet of triplets where $J_{X-H} \approx J_{A-X}$. In summary, each phosphorus type couples to two seemingly magnetically equivalent hydrides, giving a partial stoichiometry of "$MoH_2(PMe_2Ph)_4$" for **1**. Two rather broad infrared bands are seen at 1900 (w) and 1867 (m) cm^{-1}, which are assigned to ν_{Mo-H}.

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Table II. Fractional Coordinates and Isotropic Thermal Parameters for $[MoH_2(PMe_2Ph)_4(NCMe)_2](BF_4)_2$

	10^4x	10^4y	10^4z	$10B_{iso}$,[a] $Å^2$
Mo(1)	8756 (1)	4196[b]	9330 (1)	14
Mo(1)A	8376 (1)	1717.0 (4)	4117 (1)	15
P(1)	7577 (4)	3739 (1)	9924 (4)	16
P(2)	9538 (4)	4861 (1)	8990 (4)	15
P(3)	11157 (4)	3944 (1)	10895 (4)	21
P(4)	7373 (4)	3920 (1)	7076 (4)	18
P(1)A	7355 (4)	2199 (1)	4834 (4)	17
P(2)A	9029 (4)	1047 (1)	3701 (4)	17
P(3)A	10850 (4)	1900 (1)	5819 (4)	18
P(4)A	7090 (4)	2030 (1)	1924 (4)	17
N(1)	9294 (12)	4489 (4)	11082 (11)	20
N(2)	6898 (12)	4568 (4)	8439 (11)	21
C(1)	9545 (14)	4648 (4)	11981 (13)	17 (2)
C(2)	9824 (15)	4869 (5)	13121 (14)	23 (3)
C(3)	5948 (14)	4768 (4)	8039 (13)	18 (3)
C(4)	4679 (15)	5001 (5)	7521 (14)	24 (3)
C(5)	8596 (15)	3573 (5)	11631 (14)	24 (3)
C(6)	6118 (14)	3982 (4)	9712 (13)	19 (3)
C(7)	6851 (13)	3249 (4)	9099 (12)	15 (2)
C(8)	5456 (16)	3153 (5)	8403 (15)	27 (3)
C(9)	4988 (15)	2767 (5)	7872 (15)	25 (3)
C(10)	5919 (15)	2487 (5)	8001 (14)	23 (3)
C(11)	7307 (15)	2584 (4)	8694 (14)	21 (3)
C(12)	7753 (14)	2977 (4)	9227 (14)	19 (3)
C(13)	8416 (15)	5089 (5)	7333 (14)	24 (3)
C(14)	9533 (15)	5269 (5)	9945 (15)	26 (3)
C(15)	11255 (14)	4907 (4)	9401 (13)	18 (2)
C(16)	12287 (15)	5159 (5)	10432 (14)	23 (3)
C(17)	13576 (15)	5170 (5)	10726 (14)	22 (3)
C(18)	13879 (15)	4934 (5)	10067 (15)	26 (3)
C(19)	12852 (15)	4697 (5)	9030 (14)	24 (3)
C(20)	11524 (15)	4689 (4)	8706 (14)	21 (3)
C(21)	11877 (18)	3742 (6)	10131 (18)	39 (4)
C(22)	12511 (19)	4302 (6)	12032 (18)	41 (4)
C(23)	11553 (14)	3545 (4)	12042 (13)	19 (3)
C(24)	12010 (14)	3637 (4)	13314 (14)	21 (3)
C(25)	12365 (17)	3329 (5)	14213 (16)	31 (3)
C(26)	12279 (18)	2939 (5)	13832 (17)	34 (3)
C(27)	11795 (16)	2833 (5)	12585 (15)	29 (3)
C(28)	11439 (14)	3136 (4)	11682 (14)	20 (3)
C(29)	7972 (16)	3434 (5)	6933 (15)	28 (3)
C(30)	5532 (17)	3812 (5)	6267 (16)	31 (3)
C(31)	7238 (13)	4214 (5)	5807 (12)	19 (2)
C(32)	6104 (15)	4470 (5)	5001 (14)	24 (3)
C(33)	6016 (16)	4698 (5)	4052 (15)	28 (3)
C(34)	7038 (16)	4674 (5)	3911 (15)	28 (3)
C(35)	8194 (15)	4429 (5)	4764 (15)	25 (3)
C(36)	8295 (14)	4197 (5)	5710 (14)	26 (3)
N(1)A	8727 (12)	1409 (3)	5771 (12)	21
N(2)A	6402 (11)	1406 (3)	3094 (10)	16
C(1)A	8927 (14)	1263 (4)	6682 (13)	17 (2)
C(2)A	9141 (16)	1086 (5)	7797 (15)	28 (3)
C(3)A	5358 (15)	1259 (5)	2608 (14)	21 (3)
C(4)A	4024 (16)	1064 (5)	2047 (15)	28 (3)
C(5)A	8473 (15)	2337 (5)	6594 (14)	22 (3)
C(6)A	5884 (16)	1981 (5)	4642 (16)	30 (3)
C(7)A	6746 (15)	2700 (5)	4135 (14)	22 (3)
C(8)A	5392 (15)	2830 (5)	3547 (14)	24 (3)
C(9)A	5038 (17)	3241 (5)	3133 (17)	35 (3)
C(10)A	6005 (17)	3496 (5)	3238 (16)	32 (3)
C(11)A	7321 (14)	3347 (4)	3772 (14)	20 (3)
C(12)A	7707 (15)	2959 (5)	4243 (14)	22 (3)
C(13)A	7788 (15)	813 (5)	2059 (14)	23 (3)
C(14)A	9135 (14)	657 (5)	4739 (14)	22 (3)
C(15)A	10664 (14)	1011 (4)	3952 (13)	19 (3)
C(16)A	11836 (13)	821 (4)	5040 (13)	16 (2)
C(17)A	13069 (15)	826 (5)	5268 (14)	22 (3)
C(18)A	13188 (15)	1026 (5)	4394 (15)	26 (3)
C(19)A	12004 (16)	1226 (5)	3261 (16)	30 (3)
C(20)A	10743 (15)	1213 (5)	3055 (14)	23 (3)
C(21)A	11978 (17)	1916 (5)	5356 (16)	31 (3)
C(22)A	11848 (15)	1566 (5)	7257 (15)	26 (3)
C(23)A	11326 (14)	2399 (4)	6631 (13)	19 (3)
C(24)A	11856 (15)	2444 (5)	7913 (14)	23 (3)
C(25)A	12226 (18)	2831 (5)	8510 (17)	35 (3)
C(26)A	12018 (18)	3160 (5)	7737 (17)	35 (3)
C(27)A	11443 (16)	3122 (5)	6404 (15)	26 (3)
C(28)A	11108 (14)	2739 (4)	5846 (14)	20 (3)
C(29)A	7835 (15)	2493 (4)	1848 (14)	22 (3)
C(30)A	5295 (17)	2198 (5)	1134 (16)	32 (3)
C(31)A	6819 (12)	1738 (4)	599 (12)	17 (2)
C(32)A	5625 (15)	1491 (5)	−203 (14)	22 (3)
C(33)A	5421 (14)	1257 (5)	−1197 (14)	22 (3)
C(34)A	6388 (15)	1273 (5)	−1411 (14)	24 (3)
C(35)A	7583 (15)	1516 (5)	−629 (14)	25 (3)
C(36)A	7787 (13)	1748 (5)	391 (12)	19 (2)
F(1)	3020 (10)	463 (4)	7898 (10)	28
F(2)	4197 (12)	703 (4)	9953 (12)	37
F(3)	3043 (12)	116 (4)	9399 (11)	38
F(4)	1845 (12)	694 (4)	8547 (13)	44
F(1)A	3726 (11)	5572 (4)	3383 (10)	38
F(2)A	3498 (15)	5738 (5)	4922 (13)	67
F(3)A	4796 (14)	5223 (5)	5249 (13)	59
F(4)A	2447 (18)	5204 (6)	3673 (20)	100
F(1)B	832 (11)	4017 (3)	4775 (11)	36
F(2)B	1674 (11)	4578 (3)	6038 (10)	30
F(3)B	3003 (14)	4027 (5)	6651 (15)	73
F(4)B	1486 (20)	4032 (6)	6853 (20)	93
F(1)C	2742 (14)	1988 (6)	11622 (15)	77
F(2)C	1508 (18)	1755 (5)	9580 (13)	77
F(3)C	1099 (21)	2387 (5)	9965 (16)	93
F(4)C	586 (19)	1884 (6)	10572 (21)	108
B(1)	3037 (23)	492 (7)	8976 (21)	24
B(1)A	3608 (19)	5427 (8)	4304 (20)	22
B(1)B	1852 (29)	4197 (8)	5875 (28)	60
B(1)C	1441 (25)	2014 (8)	10411 (22)	34

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, *12,* 609. [b] This parameter was not varied.

Compound **1** shows a B–F stretching frequency at 1050 cm^{-1} in the infrared spectrum, consistent with the presence of BF_4^- units. The diamagnetism implied by the NMR results requires an even B:Mo ratio *if* **1** may be assumed to be monomeric; a B:Mo ratio of 2:1 is indicated by the experimentally determined reaction stoichiometry. However, the resultant formula, $MoH_2(PMe_2Ph)_4(BF_4)_2$, is inconsistent with our inability to produce samples of **1** whose ^1H NMR spectrum is free of significant amounts of CH_3CN, even after prolonged pumping on the solid reaction product. A point of confusion arose in that CD_3CN was the preferred NMR solvent (**1** is insoluble in THF); under these conditions, the CH_3CN resonances in samples of **1** were consistently at the chemical shift of *free* CH_3CN. Moreover, crystalline samples of **1** exhibit C≡N stretches at 2310 and 2275 cm^{-1} (in KBr), the former being significantly different from that of free acetonitrile. Coordination of the cyanide group is known to raise ν_{CN}. We sought confirmation of the deductions from spectroscopic data and a clarification of the question of the "residual" acetonitrile via a crystallographic study.

Structure of $[MoH_2(PMe_2Ph)_4(NCMe)_2](BF_4)_2$. The X-ray study of **1** shows it to be composed of monomeric dications, $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$, containing two coordinated (linear) acetonitrile molecules. The crystal contains two independent cations in the asymmetric unit (Figure 1). Because of the large number of independent positional parameters and the noncentric space group, no hydrogens were located. The structural study shows that the cation bears charge 2+ since two BF_4^- ions were located for each molybdenum. Each of the two cations is chiral by virtue of the disposition of the phenyl and methyl groups (i.e., the inner coordination sphere, MoP_4N_2, is nearly achiral). However, the chirality of the two independent cations is opposite: the two cations are nearly enantiomers of each other (Figures 1 and 2). This permits

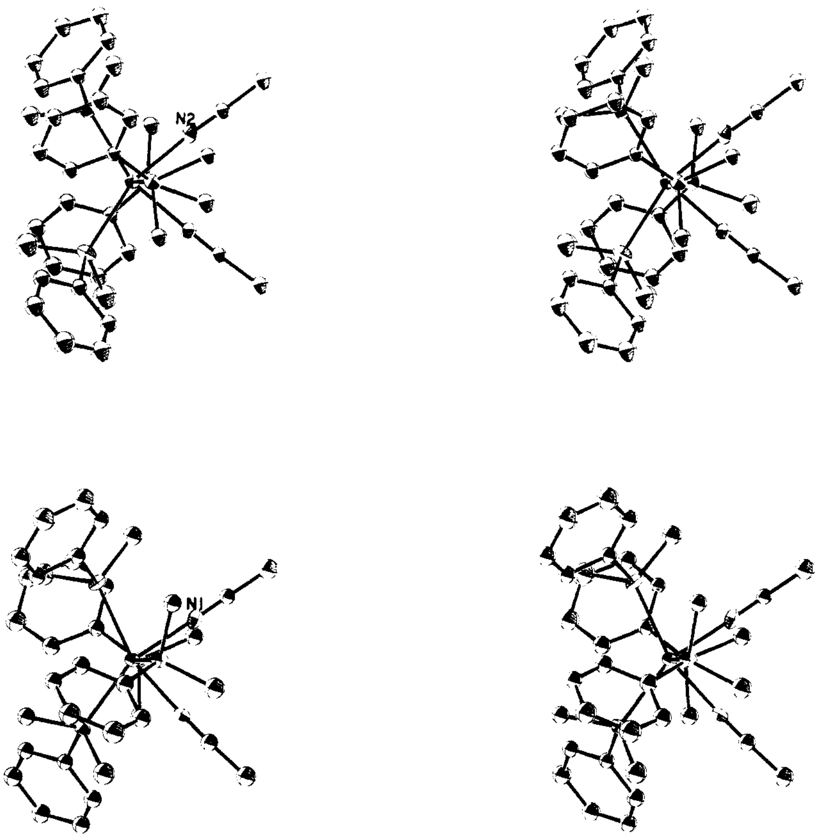


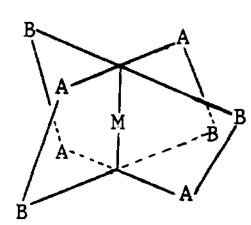
Figure 2. Stereo ORTEP views of two conformers of $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$, rotated 90° about a vertical axis from Figure 1: above, first conformer. This view is perpendicular to the P(3)P(4)N(1)N(2) trapezoid, with the approximate C_2 axis horizontal.

Table III. Bond Distances (Å) for the Two Cations in $[MoH_2(PMe_2Ph)_4(NCMe)_2](BF_4)_2$

	1st cation	2nd cation ("A")
Mo(1)-P(1)	2.539 (4)	2.553 (4)
Mo(1)-P(2)	2.565 (4)	2.545 (4)
Mo(1)-P(3)	2.472 (4)	2.486 (4)
Mo(1)-P(4)	2.479 (4)	2.475 (4)
Mo(1)-N(1)	2.174 (12)	2.175 (13)
Mo(1)-N(2)	2.198 (12)	2.177 (11)
P(1)-C(5)	1.832 (16)	1.853 (15)
P(1)-C(6)	1.832 (14)	1.824 (17)
P(1)-C(7)	1.853 (15)	1.824 (17)
P(2)-C(13)	1.853 (16)	1.858 (15)
P(2)-C(14)	1.847 (17)	1.821 (16)
P(2)-C(15)	1.842 (14)	1.838 (14)
P(3)-C(21)	1.830 (18)	1.834 (17)
P(3)-C(22)	1.825 (19)	1.843 (16)
P(3)-C(23)	1.824 (15)	1.860 (15)
P(4)-C(29)	1.835 (18)	1.832 (16)
P(4)-C(30)	1.850 (16)	1.856 (17)
P(4)-C(31)	1.841 (15)	1.824 (14)
N(1)-C(1)	1.139 (17)	1.158 (17)
N(2)-C(3)	1.153 (17)	1.136 (17)
C(1)-C(2)	1.496 (20)	1.434 (21)
C(3)-C(4)	1.483 (20)	1.472 (21)

the conclusion that the Ph and Me conformation adopted, because it (or its enantiomer) is present in both cations, is dictated by nonbonding interactions within the cation and not by lattice-packing forces. The efficiency of the intracationic packing is evident in Figure 3, which shows the near-C_2 rotational symmetry of the entire cation, including phenyl and methyl groups. As a quantitative assessment of the similarity of the two independent cations, we have performed a "best molecular fit" calculation[18] of the enantiomer of the second conformer (denoted "A") to the first conformer. Atom positions in the two MoP_4N_2 units differ by less than 0.08 Å.

The inner coordination spheres of the cations are composed of two nearly orthogonal planes. The atoms Mo, P(3), P(4), N(1), and N(2) are coplanar to within ±0.14 Å. The angles between planes MoP(3)P(4) and MoP(1)P(2) in the two cations are 94.3 and 93.9° (angles employing the expanded plane MoP(3)P(4)N(1)N(2) are 91.7 and 88.5°). The two metal-bound hydrogens (established by ^{31}P and ^1H NMR) bring the coordination number to 8. Two orthogonal ligand planes are characteristic of a dodecahedral coordination geometry, this polyhedron also being the one adopted by $MoH_4(PMePh_2)_4$.[19] The dodecahedron is characterized by two orthogonal trapezoidal arrays of ligands. In $MoH_2(PMe_2Ph)_4(NCMe)^{2+}$, one (planar) trapezoid is composed of P(3), P(4), and two MeCN molecules, with the former occupying the more sterically accommodating B sites (see I).[20]



I

The second trapezoid has P(1) and P(2) in the B sites; the two hydride ligands should lie at A sites in the horizontal plane viewed edge-on in Figures 1–3. It is evident from Figure 3 that there are two "holes" in the coordination sphere through which the central (hatched) molybdenum is visible, and it is in these "holes" that the hydride hydrogens must reside. The

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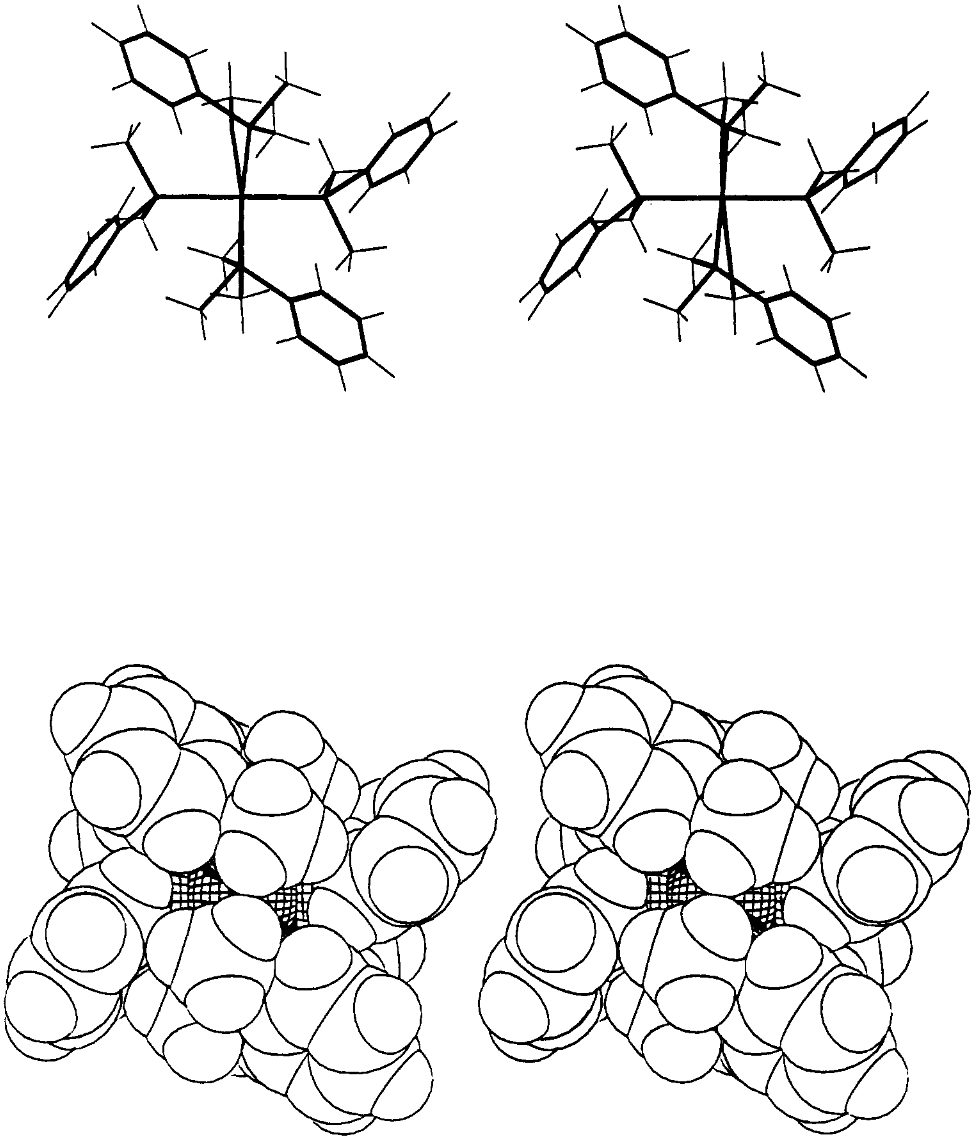

Figure 3. Stereo stick and space-filling drawings of the first conformer of $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$, viewed as in Figure 1. Hydride hydrogens are omitted, and hydrogens bound to carbon are placed in idealized positions by using a C–H distance of 1.08 Å.

molybdenum is not visible from any other perspective of a space-filling model.

The compounds $MoH_4(PMePh_2)_4$[19] and $WH_4(PEtPh_2)_4$[21] provide useful standards for comparison to the structure of **1**. These have a P–M–P angle within the trapezoid of 139.1–144.1°. In **1**, this angle (in the $MoH_2P(1)P(2)$ plane) is 157°, in response to the presence of the nearby (larger) acetonitrile ligands in the orthogonal plane. In the $Mo(NCMe)_2P(3)P(4)$ plane this angle is reduced to 117°, a predictable response to the larger MeCN ligands at the A sites of this trapezoid. Both angles are large enough to yield P–Me triplets in the ^1H NMR. In $MoH_4(PMePh_2)_4$, the angle H–Mo–H between A sites in a trapezoid is 60°, while the angle N(1)–Mo–N(2) in **1** is 81°.

The Mo–P distances in both independent cations of **1** show systematic differences in the two orthogonal planes: those in the P_2H_2 plane average 2.551 Å, while those in the P_2N_2 plane average 2.478 Å. While these are expected to differ in the C_2 (or C_{2v}) symmetry of the coordination sphere of **1**, the significance of this observation is unclear since both of the potentially more symmetric species $MoH_4(PMePh_2)_4$ and $WH_4(PEtPh_2)_4$ show *two* types of M–P distances, differing by 0.06–0.07 Å. We attribute these latter inequalities to the same origin as the slight nonplanarity of the trapezoids (Figure 1) in **1**: torsional distortion caused by packing of the non-C_{3v} substitution pattern on the PRR'_2 phosphines. This is evident in the Mo–P–C angles of **1**, which are consistently larger (by as much as 10°) to the phenyl group than to the methyl groups; this has the effect of orienting the phenyl groups in a more radial fashion, thus minimizing their intracationic steric influence. Such distortions are not found in less crowded PMe_2Ph complexes.[22]

Subsequent to the discovery of coordinated MeCN by X-ray diffraction, we have observed a ^1H resonance in samples of **1** at δ 2.37 in CD_2Cl_2 (δ 2.56 in acetone-d_6); these we assign to coordinated acetonitrile.

Acidolysis. The above product of 2-electron oxidation of $MoH_4(PMe_2Ph)_4$ is formally the result of the replacement of two hydr*ide* ligands by two molecules of acetonitrile. Hydride abstraction is also the anticipated result of acidolysis of a M–H bond (eq 2), and we therefore examined this reaction. The

$$MH + H^+ \rightarrow M^+ + H_2 \qquad (2)$$

acid selected was commercial "$HBF_4{\cdot}Et_2O$", which probably

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[21] Lobkovskii, E. B.; Makhaev, V. D.; Borisov, A. P.; Semenenko, K. N. *J. Struct. Chem.* (*Engl. Transl.*) **1980**, *20*, 812.

[22] E.g., $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$: Trimarchi, M.; Huffman, J. C., manuscript in preparation.

Table IV. Bond Angles (Deg) for the Two Cations in $[MoH_2(PMe_2Ph)_4(NCMe)_2](BF_4)_2$

	1st cation	2nd cation ("A")
P(1)-Mo(1)-P(2)	157.0 (1)	157.6 (1)
P(1)-Mo(1)-P(3)	99.6 (1)	97.6 (1)
P(1)-Mo(1)-P(4)	92.2 (1)	92.9 (1)
P(1)-Mo(1)-N(1)	78.8 (3)	76.8 (3)
P(1)-Mo(1)-N(2)	83.7 (3)	84.4 (3)
P(2)-Mo(1)-P(3)	92.8 (1)	91.6 (1)
P(2)-Mo(1)-P(4)	99.8 (1)	100.6 (1)
P(2)-Mo(1)-N(1)	83.8 (3)	84.5 (3)
P(2)-Mo(1)-N(2)	78.6 (3)	80.5 (3)
P(3)-Mo(1)-P(4)	115.9 (1)	118.3 (1)
P(3)-Mo(1)-N(1)	82.1 (3)	81.8 (3)
P(3)-Mo(1)-N(2)	161.4 (3)	161.3 (3)
P(4)-Mo(1)-N(1)	161.2 (3)	158.9 (3)
P(4)-Mo(1)-N(2)	82.1 (3)	80.0 (3)
N(1)-Mo(1)-N(2)	80.6 (4)	80.7 (4)
Mo(1)-P(1)-C(5)	117.6 (5)	116.9 (5)
Mo(1)-P(1)-C(6)	112.8 (5)	112.2 (6)
Mo(1)-P(1)-C(7)	120.9 (5)	122.4 (5)
C(5)-P(1)-C(6)	100.5 (7)	100.2 (7)
C(5)-P(1)-C(7)	98.9 (7)	98.6 (7)
C(6)-P(1)-C(7)	103.1 (6)	103.4 (7)
Mo(1)-P(2)-C(13)	117.9 (5)	118.1 (5)
Mo(1)-P(2)-C(14)	111.0 (5)	110.7 (5)
Mo(1)-P(2)-C(15)	120.7 (5)	118.6 (5)
C(13)-P(2)-C(14)	99.8 (7)	100.5 (7)
C(13)-P(2)-C(15)	101.1 (7)	101.7 (7)
C(14)-P(2)-C(15)	103.4 (7)	105.1 (7)
Mo(1)-P(3)-C(21)	114.6 (6)	118.5 (5)
Mo(1)-P(3)-C(22)	117.9 (6)	115.5 (5)
Mo(1)-P(3)-C(23)	119.6 (5)	120.2 (5)
C(21)-P(3)-C(22)	99.9 (8)	101.0 (7)
C(21)-P(3)-C(23)	101.9 (8)	97.3 (7)
C(22)-P(3)-C(23)	99.8 (8)	100.8 (7)
Mo(1)-P(4)-C(29)	115.1 (5)	115.9 (5)
Mo(1)-P(4)-C(30)	116.2 (5)	116.8 (6)
Mo(1)-P(4)-C(31)	118.5 (5)	118.4 (5)
C(29)-P(4)-C(30)	101.6 (8)	100.5 (7)
C(29)-P(4)-C(31)	101.2 (7)	101.6 (7)
C(30)-P(4)-C(31)	101.6 (7)	100.7 (7)
Mo(1)-N(1)-C(1)	178.2 (11)	176.7 (12)
Mo(1)-N(2)-C(3)	176.3 (11)	175.5 (11)
N(1)-C(1)-C(2)	177.6 (15)	178.6 (15)
N(2)-C(3)-C(4)	176.3 (15)	177.0 (15)

exists as the dialkyloxonium salt, $[HEt_2O^+]BF_4$.[23,24] This has the advantage that the counterion is a very weak ligand, as is the conjugate base (Et_2O) of the cationic acid.

Treatment of an acetonitrile slurry of $MoH_4(PMe_2Ph)_4$ with excess $HBF_4{\cdot}Et_2O$ at 25 °C gives quantitative conversion (by ^1H and ^{31}P NMR) to $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$, established by the identity of its ^{31}P and ^1H NMR spectra with authentic **1** from silver oxidation. A moderate excess of acid has no further effect over a period of 1–2 h at 25 °C. This result represents a convenient alternate synthesis of **1** but contrasts with the result[25] in THF that HBF_4 converts $MoH_4(PMePh_2)_4$ to a product characterized as "$MoH_3(PMePh_2)_3BF_4$". In view of the difference of the phosphine employed by previous workers (in THF)[25] and by us, we investigated the acidolysis of $MoH_4(PMePh_2)_4$,[16] but in acetonitrile. Treatment of an acetonitrile solution of $MoH_4(PMePh_2)_4$ with excess $HBF_4{\cdot}Et_2O$ gives immediate gas evolution at 25 °C. The proton NMR of the resulting solution shows a hydride quartet and one phosphine methyl "filled-in doublet"; the integral of these resonances is consistent with a $MoH_2(PMePh_2)_3$ stoichiometry. The $^{31}P\{^1H\}$ NMR spectrum of this solution shows a singlet for coordinated $PMePh_2$ (at +35 and −89 °C) and another singlet (of one-third the intensity of the other signal) at δ 2.4. Selective proton decoupling of only phenyl and methyl protons at relatively low decoupling power converts the coordinated $PMePh_2$ signal to a triplet, while the other singlet becomes a doublet with an *apparent* J value of 380 Hz. The latter we attribute to $HPMePh_2^+$. Taken together, these data indicate reaction 3.

$$MoH_4(PMePh_2)_4 + 3H^+ \xrightarrow{MeCN} MoH_2(PMePh_2)_3(NCMe)_n^{2+} + HPMePh_2^+ + 2H_2 \quad (3)$$

The proton NMR of the product mixture, dissolved in CD_3CN, shows a resonance for coordinated MeCN. The intensity of this resonance is less than that expected for $n = 3$ in eq 3; however, a small CH_3CN peak is observed at the chemical shift of free acetonitrile. This suggests that free and coordinated nitriles exchange in $MoH_2(PMePh_2)_3(NCMe)_3^{2+}$ but at a reduced rate compared to that in $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$. For comparison to eq 3, we also performed the $AgBF_4$ oxidation of $MoH_4(PMePh_2)_4$. When these are reacted in a 2:1 ratio in MeCN, gas evolves from the solution, and the molybdenum product has ^1H and ^{31}P NMR spectra identical with those observed after acidolysis (eq 4).

$$MoH_4(PMePh_2)_4 + 2Ag^+ \xrightarrow{MeCN} H_2 + MoH_2(PMePh_2)_3(NCMe)_3^{2+} + 2Ag^0 + PMePh_2 \quad (4)$$

The above results indicate a marked influence of the phosphine on the course of both oxidation and acidolysis reactions. To better understand this, we refluxed (81 °C) a solution of $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$ (from $AgBF_4$) in CD_3CN for 0.5 h. The ^1H NMR spectrum of this solution is consistent with the production of $MoH_2(PMe_2Ph)_3(NCMe)_3^{2+}$. It consists of a hydride quartet and a "filled-in doublet" for the phosphine methyl groups; also seen is free PMe_2Ph. The $^{31}P\{^1H\}$ spectrum of this solution shows (in addition to free PMe_2Ph) a singlet (δ 26.5) that becomes a triplet (apparent J_{P-Mo-H} = 38 Hz) in the selectively hydride-coupled spectrum (eq 5). Equation 5 also occurs over a period of several hours in CH_3CN at 25 °C.

$$MoH_2(PMe_2Ph)_4(NCMe)_2^{2+} \xrightarrow[MeCN]{\Delta} MoH_2(PMe_2Ph)_3(NCMe)_3^{2+} + PMe_2Ph \quad (5)$$

Discussion

Two equivalents of either a strong protic acid or Ag^+, in the presence of the weakly coordinating anion BF_4^-, effects the same reaction on an acetonitrile solution of MoH_4P_4 (P = PMe_2Ph, $PMePh_2$). The products are $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$ and $MoH_2(PMePh_2)_3(NCMe)_3^{2+}$, respectively. The dependence of the product formed upon the identity of the phosphine appears to be a matter of kinetics, since the former compound undergoes substitution of one PMe_2Ph ligand by acetonitrile on brief refluxing or, more slowly, at 25 °C in neat acetonitrile. Steric effects are perhaps sufficient to dictate facile loss of one phosphine from the proposed primary product $MoH_2(PMePh_2)_4(NCMe)_2^{2+}$. The spectroscopic properties of $MoH_2(PMePh_2)_3(NCMe)_3^{2+}$ suggest fluxionality, and its geometric structure thus remains unknown. The observation that acidolysis *in THF* yields the *tri*hydride $MoH_3(PMePh_2)_3BF_4$[25] shows the considerable influence of the coordinating solvent acetonitrile.

The cation $MoH_2(PMe_2Ph)_4(NCMe)_2^{2+}$ shows no rapid interchange between the two inequivalent phosphine environments at ambient temperature. The +16 °C ^1H NMR spectrum of the hydride protons is, however, deceptively simple in being a triplet of triplets. In the solid-state structure, the

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hydride nuclei are the magnetically inequivalent H and H′ portions of an $HH'A_2XX'$ spin system. Although the −35 °C ^1H NMR spectrum at 220 MHz shows some evidence for transformation to the more complex pattern of an $HH'A_2XX'$ spin system, we have made no effort to characterize the dynamic process more fully. In addition to the obvious wholly intramolecular mechanism, a process dissociative in MeCN also warrants consideration.

The consistent pattern from the current work is that the electrophiles $AgBF_4$ and $HBF_4{\cdot}Et_2O$ are both useful reagents for producing (the same) cationic, but diamagnetic, product, with incorporation of any available ligands. When performed in acetonitrile solvent, the reactions do not yield truly unsaturated (16-electron) species, nor do they yield complexes with coordinated BF_4^-.[26] Instead, one nitrile assumes the place of each abstracted H^-, to yield a product of unaltered valence-electron count. The utility of this synthetic method lies in the lability observed for the nitrile ligands.[27]

As mentioned above, electrophilic attack on MoH_4P_4 does not yield an unsaturated complex when acetonitrile (chosen to dissolve both reagents) is the solvent. Neither do they yield an *isolable* radical cationic hydride. The following isolable paramagnetic hydrides have been claimed: $HFe(dppe)_2$,[28] $[HFeCl(dppe)_2]BF_4$,[28] and $HCoL_4^+$.[29] The following paramagnetic hydrides have been characterized by low-temperature ESR and electrochemical techniques: $HFe_2(CO)_8$,[30] $HFe_3(CO)_{11}$,[30] Cp_2NbH_2,[31] $Ta(dmpe)_2H_4$,[31] and $Cp_2W(Ph)H^+$;[32] they are not sufficiently stable to permit isolation. Prior to discussion of possible reasons for not isolating $MoH_4P_4^{+}\cdot$, some comment on the acidolysis reaction is appropriate.

The mechanism of the initial step of the acidolysis (eq 6)

$$MoH_4P_4 + HOEt_2^+ \rightarrow [MoH_5P_4^+] + OEt_2 \rightarrow [MoH_3P_4^+] + H_2 \quad (6)$$

is perhaps the least controversial of the reactions reported here. The postulated species $MoH_5P_4^+$ (species in square brackets have not been observed here) is analogous to the isolable species $WH_5(PMePh_2)_4^+$,[25] tungsten being more resistant than molybdenum to the reduction step that is implied by elimination of H_2.[33] Here, as in what follows, a 16-electron species such as $MoH_3P_4^+$ will probably bind 1 mol of acetonitrile. The next step in the reaction is less clear. Although protonation of the cation $MoH_3P_4(NCMe)^+$ is not expected to be as favorable as eq 6, such a reaction, followed by reductive elimination of hydrogen and solvent coordination, does yield the observed $MoH_2P_4(NCMe)_2^{2+}$. Protonation (HBF_4) of the cation $Rh(dppe)^+$ has been shown[34] to produce *fac*-$RhH(dppe)(solvent)_3^{2+}$. Concentrated HCl converts $(C_6H_6)Mo(PEt_3)_3H^+$ into $(C_6H_6)Mo(PEt_3)_3H_2^{2+}$.[35]

The $AgBF_4$ oxidation offers a greater variety of mechanistic possibilities, in part because we observe only the net result of loss of not one but two ligands. Conventional mechanistic options include outer-sphere and inner-sphere (Mo–(μ-H)–Ag) paths. However, recent work by Lauher[36] makes it conceivable that the initial encounter of the reactants is *not* simply electron transfer. Lauher[36] has shown that the R_3PAu^+ unit is structurally analogous to the proton (or, more generally, to monovalent ligands which are capable of occupying both bridging and terminal sites). The generality of the concept for group 1B is evident in the work of the Bradley group[37] and the Chini group,[38] each of whom independently established $(MeCN)Cu^+$ as a capping unit for M_3 triangles. The appropriate application to the case at hand is that $(MeCN)Ag^+$ may bind to MoH_4P_4 to give a transient adduct $(MeCN)Ag{\cdot}MoH_4P_4^+$, which then reductively eliminates $(MeCN)AgH$ to leave $MoH_3P_4^+$, the latter being identical with the primary product of acidolysis. In this scheme, Ag^+ is a "hydride abstractor" just as H^+ is in eq 6. The generation of H_2 and Ag^0 then originates from the decomposition of $(MeCN)AgH$. Formation of such an adduct is observed[39] in the 2:1 reaction of $CpRhCO(PPh_3)$ with $AgPF_6$, to give diamagnetic $CpOC(Ph_3P)Rh{\rightarrow}Ag{\leftarrow}Rh(PPh_3)COCp^+$. The complex (triars)$AgCo(CO)_4$ contains a silver/cobalt bond devoid of bridging ligands.[40]

Within the realm of reactions originating in outer-sphere electron transfer to give Ag^0 and the radical $MoH_4P_4^+$, the simplest subsequent event is a second electron transfer. Moreover, since we observed that equimolar MoH_4P_4 and $AgBF_4$ simply result in 50% conversion to the same dicationic product (with recovery of 50% of the MoH_4P_4), any second 1-electron oxidation must be faster than the oxidation of MoH_4P_4 itself. Another fate for the postulated cation $MoH_4P_4^{+}\cdot$ is disproportionation (eq 7) followed by reductive

$$2[MoH_4P_4^{+}\cdot] \rightarrow MoH_4P_4 + [MoH_4P_4^{2+}] \quad (7)$$

$$[MoH_4P_4^{2+}] \xrightarrow[+NCMe]{-H_2} \text{product}$$

elimination of H_2 from Mo(VI). Finally, the work of Klingler and Kochi[32] indicates that paramagnetic hydride cations may transfer H^+ to a suitable acceptor. In the case at hand, MoH_4P_4 is a plausible acceptor (eq 8). Such a proposal

$$\begin{tikzcd}[MoH_4P_4^{+}\cdot] + MoH_4P_4 \arrow[r] & {[MoH_3P_4\cdot] + [MoH_5P_4^+]} \arrow[d] \\ & {[MoH_3P_4^+] + H_2 \quad (8)}\end{tikzcd}$$

frustrates further speculation, since we now have two different metal hydride transients awaiting further oxidation. However, it is worth emphasizing the difference between the present results and those of Kochi and Klingler. They were able to produce the 1-electron-oxidized species $Cp_2WH_2^+$, which they found not to lose H_2 but rather H^+. The kinetics of our system have prevented interception of the primary product of the Ag^+ reaction with MoH_4P_4 (which is *perhaps* the 1-electron-oxidized $MoH_4P_4^{+}\cdot$), and the *overall* (2-electron) reaction that was observed produces H_2, not H^+.

While we are continuing to examine the mechanism of the silver oxidation of MoH_4P_4, its stoichiometric similarity to acidolysis deserves notice. As shown by eq 9 and 10 (S =

$$MoH_4P_4 + 2Ag^+ \rightarrow MoH_2P_nS_{6-n}^{2+} + H_2 + 2Ag^0 \quad (9)$$

$$MoH_4P_4 + 2H^+ \rightarrow MoH_2P_nS_{6-n}^{2+} + 2H_2 \quad (10)$$

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solvent), each electrophile cleanly produces the same molybdenum complex, being the product of formal abstraction of two H^- units from MoH_4P_4. In this superficial sense, the silver reaction resembles chloride abstraction using Ag^+, with the difference being the relative stability of AgCl and AgH.

Our future work will explore the limits of weakly coordinating solvents, S, which will still permit eq 9 and 10.

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Registry No. 1, 83096-28-0; $MoH_4(PMe_2Ph)_4$, 40209-71-0; $[MoH_2(PMe_2Ph)_3(CH_3CN)_3](BF_4)_2$, 83096-30-4; $MoH_4(PMePh_2)_4$, 32109-07-2; $[MoH_2(PMePh_2)_3(CH_3CN)_3](BF_4)_2$, 83096-32-6; $MoCl_3(THF)_3$, 31355-55-2; $HBF_4{\cdot}Et_2O$, 67969-82-8; $AgBF_4$, 14104-20-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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Some Cationic Bis(hydrido)-Bridged Platinum–Iridium Complexes

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The preparation of some bimetallic hydrido-bridged cationic species of the type $[L'RPt(\mu\text{-}H)_2IrHL_2L']^+$ (for L = L′ = PEt_3, R = H (3) and Ph (4); for L = PEt_3 and L′ = $P(i\text{-}Pr)_3$, R = H (5)), from *trans*-$[PtR(MeOH)L_2]^+$ and $[IrH_5L_2]$ is described. The reaction of 3 with CO gives $[IrH_2(CO)(PEt_3)_3]^+$ and some Pt/CO/PEt_3 clusters, with C_2H_4 gives $[(PEt_3)(Et)Pt(\mu\text{-}H)_2IrH(PEt_3)_3]^+$ (**6**), and with H_2 gives $[(PEt_3)_2Pt(\mu\text{-}H)_2IrH_2(PEt_3)_2]^+$ (**8**). The reaction of **6** and H_2 gives C_2H_6 and **8**. The ^1H, ^{31}P, and some ^{13}C NMR data are reported and used for structural assignment.

Introduction

While mono(hydrido) complexes of platinum(II) have been known for a considerable time,[2,3] the isolation of bis(hydrido) complexes of the types *trans*-$[PtH_2L_2]$ (L = tertiary phosphine)[4-7] and *cis*-$[PtH_2(LL)]$ (LL = chelating di(tertiary phosphine) having bulky substituents on the phosphorus atom)[8,9] has been reported more recently. Several types of hydrido-bridged binuclear platinum complexes have also been described during the last three years.[10-17] We report here the preparation, spectroscopic characterization, and some reactivity studies of a class of bimetallic platinum–iridium complexes containing double hydrido bridges. A preliminary account of some of this work has appeared elsewhere.[18]

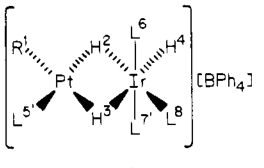
Results and Discussion

Preparative Studies. The hydrido-bridged bimetallic platinum–iridium complexes **3–5** were prepared according to eq 1. This synthetic route is an extension of a general reaction

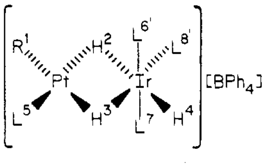
$$trans\text{-}[PtR(MeOH)L_2]^+ + [IrH_5L'_2] \rightarrow \mathbf{3\text{–}5} + H_2 + MeOH \quad (1)$$

1a, R = H, L = PEt_3
b, R = H, L = $P(i\text{-}Pr)_3$
c, R = Ph, L = PEt_3

2a, L′ = PEt_3
b, L′ = $P(i\text{-}Pr)_3$



3a, R = H, L = L′ = PEt_3
4a, R = Ph, L = L′ = PEt_3
5a, R = H, L = PEt_3; L′ = $P(i\text{-}Pr)_3$
6a, R = C_2H_5, L = L′ = Et_3P



3b, R = H, L = L′ = PEt_3
4b, R = Ph, L = L′ = PEt_3
6b, R = C_2H_5, L = L′ = PEt_3

that has been used in this laboratory to prepare binuclear hydrido-bridged complexes: labile, coordinated solvent molecules can easily be displaced, not only by two-electron donors[19] but also by hydrido complexes, giving bimetallic hydrido-

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