$^{95}M_0$ NMR INVESTIGATION ON CATIONIC [C₅H₅M₀(CO)₂L₂]BF₄ COMPLEXES (L = GROUP 15 DONOR LIGANDS*

HANS SCHUMANN^{†‡}

Department of Chemistry, University of Utah, Salt Lake City, UT 84112, U.S.A.

and

JOHN H. ENEMARK[†] and MICHAEL J. LABARRE

Department of Chemistry, University of Arizona, Tucson, AZ 85721, U.S.A.

and

MICHAEL BRUCK and PAMELA WEXLER

Molecular Structure Laboratory, University of Arizona, Tucson, AZ 85721, U.S.A.

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Abstract—Photochemically-initiated oxidative fission of the Mo—Mo bond in $[C_5H_5Mo(CO)_3]_2$ by the ferricenium salt $[(C_5H_5)_2Fe]BF_4$ in the presence of four equivalents of L affords a good yield of $[C_5H_5Mo(CO)_2L_2]BF_4$ (L = group 15 donor ligands). ⁹⁵Mo NMR data are reported and discussed together with the NMR and IR data of new complexes. Decomposition of the title cations in polar solvents affords low yields of the corresponding $[C_5H_5Mo(CO)_3L]BF_4$ complexes. The X-ray crystal structure of $[C_5H_5Mo(CO)_3L]BF_4$ is reported. The cation has the CpML₄ piano-stool geometry.

In contrast to the well investigated cationic iron complexes $[C_5H_5Fe(CO)_{3-n}L_n]X^2$ cationic molybdenum complexes of the type $[C_5H_5M_0(CO)_{4-n}]$ $L_n|X$ have attracted much less interest.³ Known complexes of the type $[C_5H_5M_0(CO)_2L_2]X$ with L = group 15 donor ligands have been obtained by different methods: by photochemically-initiated disproportionation of $[C_5H_5Mo(CO)_3]_2$ in the presence of L (X = $[C_5H_5Mo(CO)_3]^{-}$) followed by anion exchange in some cases;⁴ from the protonation of $C_5H_5Mo(CO)_3CH_3$ with HBF₄. ether in the presence of $L = NCCH_3 (X = BF_4);^5$ from $C_5H_5Mo(CO)_3X$ (X = halide) and two equivalents of L in refluxing non-polar solvents;⁶ or from the oxidative fission of the Mo-Mo bond in $[C_5H_5Mo(CO)_3]_2$ by AgX salts $(X = BF_4 \text{ or }$

† Authors to whom correspondence should be addressed. ‡ Present address: Bensberger Str. 15A, D-5064 Rösrath, F.R.G. PF_6) in the presence of L.⁷ All these methods have the major disadvantage that they are not normally generally applicable because of special conditions, requirements for L or the price of anhydrous AgX salts. However, during our attempts to develop new routes to cationic organometallic complexes,⁸ we found a new, more general preparation of the title complexes by photochemically-initiated oxidative fission of the Mo—Mo bond in $[C_5H_5$ Mo(CO)₃]₂; by ferricenium cations in the presence of L. This method makes $[C_5H_5Mo(CO)_2$ $L_2]X$ (X = BF₄, PF₆ or SbF₆) complexes and their chemistry accessible⁹ and we now report results from a ⁹⁵Mo NMR investigation of these complexes.

EXPERIMENTAL

Materials

 $[C_5H_5Mo(CO)_3]_2$ [I (Strem)], $E(C_6H_5)_3$ [II, E = P, As, Sb (Aldrich) and E = Bi (Alfa)], PR₃

^{*} See ref. 1.

[II, R = CH₃, C₂H₅, i-C₃H₇, t-C₄H₉ (Strem), OCH₃ (Aldrich)] and $[(C_6H_5)_2PCH_2]_2$ **[II** (Aldrich)] were obtained from commercial sources and used without further purification. $[(C_5H_5)_2Fe]BF_4$ (**IV**)¹⁰ was prepared and purified as described in the literature. All reactions were conducted in oven-dried Schlenk tubes using dried and degassed solvents under nitrogen.

Instrumentation

¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on Varian XL-300 spectrometers as ca 5% solutions in dried and degassed acetone- d_6 vs internal TMS ('H and ¹³C) or external 85% H₃PO₄ (³¹P) as reference. ⁹⁵Mo NMR spectra were obtained at room temperature on a Bruker AM-500 spectrometer equipped with a broad band tunable probe (95 Mo : 32.6 MHz, 90° pulse width 35 μ s and using an aquisition delay of 34 μ s to reduce probe ringing) in CDCl₃-CH₂Cl₂ solutions (ca 0.04 M). The external standard was 2 M Na₂MoO₄ at pH 11. IR spectra, v(CO), were recorded in 1,2-Cl₂C₂H₄ solution on a Perkin-Elmer 298 IR spectrometer in 0.1 mm CaF₂ cells and were calibrated against a polystyrene standard. Microanalysis for all new complexes were carried out by Dornis und Kolbe, Mülheim (F.R.G.).

Synthesis

All $[C_5H_5Mo(CO)_2L_2]BF_4$ complexes [VI(a)-VI(i)] were obtained from the following general method. To a solution of 1.0 g (2.0 mmol) $[C_{5}H_{5}Mo(CO)_{3}]_{2}$ (I) in 40 cm³ 1,2-Cl₂C₂H₄ were added 5.0 mmol (1.25 equivalents) of II (for $L = [(C_6H_5)_2PCH_2]_2$ only 2.5 mmol) and 1.1 g (4.0 mmol) $[(C_5H_5)_2Fe]BF_4$ (IV). The resulting solution was then UV irradiated until the colour changed from red (I) to yellow-brown (VI; about 0.5 to 1.5 h). Filtration followed by concentration to 1/3 in vacuo and addition of excess ether precipitated the cationic complexes VI with yields > 90%. For further purification, the solids were washed several times with ether to remove any remaining free ligand and recrystallized from CH_2Cl_2 -ether (1/2 to 1/4) at 0°C.

Spectroscopic and analytical data for all new complexes

 $[C_5H_5Mo(CO)_2\{P(C_2H_5)_3\}_2]BF_4$ [VI(b)]. ¹H NMR : δ 5.68 [br t, C_5H_5 ; J(P, H) = 1.4 Hz], 2.19 [5 line m, PCH₂; J(H, H) = J(P, H) = 7.6 Hz], 1.22 [5 line m, CH₃ on PC₂H₅; J(H, H) = 7.6 Hz] ppm. ¹³C{¹H} NMR : δ 236.13 [t, MoCO; J(P, C) = 26 Hz], 94.14 (s, C_5H_5), 23.15 [pseudo t, PCH₂; J(P, C) = 14.7 Hz], 7.08 [d, CH₃ on PC₂H₅; J(P, C) = 4.7 Hz] ppm. ³¹P{¹H} NMR : δ 40.0 (s) ppm. IR spectrum : 1964, 1885, ν (CO), cm⁻¹. Found : C, 42.5; H, 6.6. Calc. for C₁₉H₃₅BF₄MoO₂P₂: C, 42.3; H, 6.5%.

[C₅H₅Mo(CO)₂{P(CH₃)₂C₆H₅}₂]BF₄ [VI(c)]. ¹H NMR : δ 7.74, 7.57 (m, PC₆H₅), 5.48 [t, C₅H₅; *J*(P, H) = 1.3 Hz], 2.16 [pseudo d, PCH₃; *J*(P, H) = 9.9 Hz] ppm. ¹³C{¹H} NMR : δ 234.48 [t, MoCO; *J*(P, C) = 27.0 Hz], 138.4 (br m, C-1), 131.45 (s, p-C), 130.41 [t, o-C; *J*(P, C) = 4.5 Hz], 129.58 [t, m-C; *J*(P, C) = 5.2 Hz], 94.60 (s, C₅H₅), 19.58 [pseudo t, PCH₃; *J*(P, C) = 17.7 Hz] ppm. ³¹P{¹H} NMR : δ 22.2 (s) ppm. IR spectrum : 1968, 1887, *v*(CO), cm⁻¹. Found : C, 47.8; H, 4.6. Calc. for C₂₃H₂₇ BF₄MoO₂P₂: C; 47.7; H, 4.7%.

 $[C_{5}H_{5}Mo(CO)_{2}\{P(C_{6}H_{5})_{2}CH_{3}\}_{2}]BF_{4}[VI(d)]$. ¹H NMR: δ 7.61 to 7.51 (m, 10H, PC₆H₅), 5.51 [t, C₅H₅; J(P, H) = 1.3 Hz], 2.49 [pseudo d, PCH₃; J(P, H) = 8.9 Hz] ppm. ¹³C{¹H} NMR: δ 234.16 [t, MoCO; J(P, C) = 28 Hz], 135.1 (br m, C-1), 132.35 [t, o-C; J(P, C) = 4.8 Hz], 131.85 (s, p-C), 129.57 [t, m-C; J(P, C) = 5.3 Hz], 95.41 (s, C₅H₅), 20.2 (br s, PCH₃) ppm. ³¹P{¹H} NMR: δ 38.7 (s) ppm. IR spectrum: 1975, 1896, v(CO) cm⁻¹ Found: C, 56.7; H, 4.6. Calc. for C₃₃H₃₁BF₄MoO₂P₂: C, 56.4; H, 4.4%.

[C₅H₅Mo(CO)₂{P(OCH₃)₃}₂]BF₄ [VI(i)]. ¹H NMR : δ 5.80 (br s, C₅H₅), 3.77 (br s, 9H, POCH₃) ppm. ¹³C{¹H} NMR : δ 230.66 [t, MoCO, *J*(P, Cl = 40.1 Hz], 93.87 (s, C₅H₅), 54.99 (br s, POCH₃) ppm. ³¹P{¹H} NMR : δ 177.0 (s) ppm. IR spectrum : 1929 [br, ν (CO)] cm⁻¹. Found : C, 29.0; H, 4.4. Calc. for C₁₃H₂₃BF₄MoO₈P₂: C, 28.3; H, 4.2%.

[C₅H₅Mo(CO)₂{(C₆H₅)₂PCH₂}₂]BF₄ [VI(g)]. NMR data were remeasured in acetone-d₆; for analytical data see the literature.⁹ ¹H NMR : δ 7.83 to 7.48 (m, 20H, PC₆H₅), 5.01 (s, C₅H₅), 2.42, 3.31 (each br m, 2 H, PCH₂) ppm. ¹³C{¹H} NMR : δ 238.44 [t, MoCO; J(P, C) = 13.7 Hz], 137.29, 132.22 [both t, inequivalent C-1; J(P, C) = 24.3, 25.0 Hz], 132.23, 131.53 (both s, inequivalent p-C), 133.67, 131.02 [both t, inequivalent o-C; J(P, C) = 5.2, 5.1 Hz], 130.02, 129.52 [both t, inequivalent m-C; J(P, C) = 5.3, 4.9 Hz], 95.57 (s, C₅H₅), 29.92 [t, PCH₂; J(P, C) = 21.5 Hz] ppm. ³¹P{¹H} NMR : δ 76.6 (s) ppm. IR spectrum (1,2-Cl₂C₂H₄): 1987, 1921, ν (CO), cm⁻¹.

For complete analytical and spectroscopical data for all other complexes of **VI** see the literature.^{8,9}

Crystal structure determination

A brown block-like crystal of $[C_5H_5Mo(CO)_3$ {P(C₆H₅)₃}]BF₄ (VII) suitable for X-ray crystallography with the approximate dimensions $0.50 \times 0.33 \times 0.25$ mm was obtained from the repeated recrystallization of $[C_5H_5Mo(CO)_2\{P(C_6H_5)_3\}_2]$ BF₄ from acetone-CH₂Cl₂-ether (see text).

Crystal data

 $C_{26}H_{20}BF_4MoO_3P$, monoclinic, a = 12.798(1), b = 10.302(2), c = 19.598(3) Å, $\beta = 96.55(1)^\circ$, U = 2567.1 Å³, space group $P2_1/c - C_{2h}^5$ (no. 14), Z = 4, M = 594.17, $D_c = 1.54$ g cm⁻³, $\mu = 6.1$ cm⁻¹, F(000) = 1192.

Measurements

Refined unit cell parameters were obtained by centring 25 reflections on a Syntex P2₁ diffractometer. Using the θ -2 θ scan measuring routine, 6287 independent reflections (up to $2\theta = 55^{\circ}$) were measured with Mo- K_{α} radiation (graphite crystal monochromator).

Structure analysis

The structure was solved by the Patterson heavyatom method which revealed the position of the molybdenum atom. The remaining atoms were located in succeeding difference Fourier syntheses. The structure was refined by full-matrix leastsquares. Hydrogen atoms were included but constrained to ride on the carbon atom to which they are bonded. Only the 4044 reflections which had $F_o^{-1} > 3\sigma(F_o^{-2})$ were used in the refinements, which converged to give R = 0.041 and $R_w = 0.051$. Computations were carried out on a VAX computer using SDP/VAX programs.¹¹

Final atomic and thermal parameters, structure factors together with F_o and F_c data have been deposited with the Editor as supplementary material. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Preparative and spectroscopic

The results show that the preparation of cationic $[C_5H_5Mo(CO)_2L_2]BF_4$ complexes with group 15 ligands (L) is readily achieved in high yields by oxidative fission of the Mo---Mo bond in $[C_5H_5Mo(CO)_3]_2$ by the ferricenium ion. As indicated in Scheme 1, the reaction clearly depends on the donor/acceptor properties of L: with strong donor ligands, II and I react directly to form the spectroscopically observed intermediate $[C_5H_5Mo(CO)_2L]_2$ (III)⁹ while weaker donor ligands need photochemical irradiation to form III. Oxidation of III with two equivalents of $[(C_5H_5)_2Fe]^+$ (IV) may first afford the suggested intermediate V. For V, two different structures are possible : the unsaturated 16e complex may be stabilized either by coor-



dination of the BF₄ anion [structure V(a)];¹² or by coordination of a solvent molecule, S [structure V(b)], e.g. $S = CH_2Cl_2$ or acetone.¹³ Both structures should be quite reactive and therefore react rapidly with the still present second equivalent of ligand to form cis- and/or trans- $[C_3H_3M_0(CO)_2L_2]^+$ [V(a) and V(b)]. The observed mixture of *cis/trans* isomers may arise from the intermediary of a cationic six-coordinated intermediate $[C_5H_5M_0(CO)_2L]^+$ (under the assumption that C_5H_5 occupies three coordination sites)¹⁴ prior to the formation of seven-coordinated V (only the cis form is shown). "Small" ligands (L) such as alkyl-substituted phosphanes and phosphites afford exclusively cis-disubstituted complexes of VI while sterically more demanding ligands such as aryl-substituted ligands afford mixtures of both, with a dominance of the cis isomers.15

All complexes of VI were obtained in > 90% yield as yellow-brown powders which afford yellow air stable crystals after recrystallization. The complexes are very soluble in common polar solvents such as methylene chloride, acetone or nitromethane but prolonged stirring in the weak donor solvents acetone, nitromethane or dimethylsulphoxide causes decomposition with formation of the related $[C_5H_5Mo(CO)_3(L)]BF_4$ complexes in low yield. The preparation method failed for $L = P(C_3H_7-i)_3$, $P(C_4H_9-t)_3$ and $P[N(CH_3)_2]_3$. In all these cases, only unidentified C_5H_5 - and COfree decomposition products were obtained which can be explained by their strong donor/weak acceptor properties together with their increasing size.

The spectroscopic data obtained for all new complexes of VI (see Experimental) are unexceptional and in agreement with their structure. More informative are the 95 Mo NMR data given in Table 1 (for a general introduction to 95 Mo NMR spectroscopy see reference 16).

All observed ⁹⁵Mo NMR data are found within a relatively small range between -1687 and -1470ppm as expected for mononuclear molybdenum(II) complexes with line widths $(H_{1/2})$ between 165 Hz [VI(b)] and 650 Hz [VI(d), see Figs 1 and 2]. Due to the comparable small values of ${}^{1}J({}^{95}Mo$, ^{31}P) = 133–220 Hz, these couplings are only resolved in complexes VI(b) (ca 100 Hz) and VI(i) (170 Hz). In general, all complexes except VI(j) (shift ca 300 ppm) are shifted down field by ca 150 ppm with respect to the related molybdenum complexes $cis-Mo(CO)_4L_2$ and the coupling constants ${}^{1}J({}^{95}Mo, {}^{31}P)$ are of comparable size. 16 Due to the lower symmetry of complexes of VI with respect to $cis-Mo(CO)_4L_2$ and the known influence of symmetry on the line width,¹⁶ the unresolved coupling ${}^{1}J({}^{95}Mo, {}^{31}P)$ for VI may be explained. Comparison of the chemical shift values for complexes of VI with data of other $C_5H_5Mo^{II}(CO)_2(L,L)$ complexes containing chelating carbon-nitrogen, dinitrogen or disulphur ligands (δ^{95} Mo ca - 560 to -130 ppm and $H_{1/2} = 70-160 \text{ Hz})^{17}$ show that the title cations are shielded by well over 1000 ppm. This large difference may be explained at least in part by the

Complex	Ligand	δ^{13} CCO ^{<i>a</i>} (ppm)	δ^{95} Mo(H _{1/2}) ^b (ppm) (Hz)	$v(CO)^c$ (cm ⁻¹)
VI(a)	P(CH ₃) ₃	234.8	-1580 (365)	1958
VI(b)	$P(C_2H_5)_3$	236.1	-1563 (165)	1964
VI(c)	$P(CH_{3})_{2}C_{6}H_{5}$	234.5	-1508 (590)	1968
VI(d)	$P(C_6H_5)_2CH_3$	234.2	-1467 (650)	1975
VI(e)	$P(C_6H_5)_3$	226.1	-1481 (250)	1977
VI(f)	$As(C_6H_5)_3$	225.0	-1479 (285)	1976
VI(g)	$Sb(C_6H_5)_3$	225.3	-1687 (355)	1968
VI(h)	$Bi(C_6H_5)_3$	224.3	d	1967
VI(i)	$P(OCH_3)_3$	230.7	$-1642 (195)^{e}$	(1929)
VI(j)	$[(C_6H_5)_2PCH_2]_2$	238.4	-1470 (325)	1987

Table 1. Comparison of ⁹⁵Mo NMR data with selected other spectroscopic data for [C₅H₅Mo(CO)₂L₂]BF₄ (VI)

^{*a*} Data measured in acetone- d_6 ; ± 0.1 ppm.

^b Data measured in CDCl₃-CH₂Cl₂; \pm 5 ppm.

^c Only absorption at higher wavenumbers given; $\pm 2 \text{ cm}^{-1}$.

^dNo spectrum observed due to rapid decomposition and limited solubility.

 ${}^{e}{}^{1}J({}^{95}Mo, {}^{31}P) = 170$ Hz.







better acceptor properties of the ligands used in this work.

Further comparison of 95 Mo NMR data with other spectroscopic data which are also regarded as indicative for the bonding situation Mo—L¹⁵ indicate no overall correlation with respect to a general application of 95 Mo NMR as a probe for ligand properties.

During attempts to obtain single crystals of complex VI(e) suitable for X-ray structure determination for comparison with the known structure of cation VI(a)¹⁸ by repeated crystallization from CH₂Cl₂-acetone-ether mixtures, yellow crystals were obtained. The following structure determination identified these crystals subsequently as $[C_5H_5Mo(CO)_3{P(C_6H_5)_3}]BF_4$ (VII). The formation of VII may be rationalized as the result of the labile Mo—L bond in polar solvents under partial ligand replacement [possibly via a complex such as V(b)] followed by decomposition under CO release. Part of the released CO substitutes the coordinated solvent under formation of VII. Control experiments reveal the general nature of this observation; stirring of complexes VI(c)-VI(i) in acetone or acetonitrile solution for a prolonged period of time caused extensive decomposition of complexes related to VII to be observed.

The structure of $[C_5H_5Mo(CO)_3{P(C_6H_5)_3}]BF_4$ (VII)

As shown in Fig. 3, this cation belongs to the class of $C_5H_5MoL_4$ complexes with a four-legged piano-stool geometry around molybdenum for which a wide series of structural determinations were performed¹⁹ and theoretical aspects discussed in detail.²⁰ For comparison, selected bond lengths and bond angles are given in Table 2 together with those for the related pentamethylcyclopentadienyl complex $[C_5(CH_3)_5Mo(CO)_3[P(C_6H_5)_3]]^+$.²¹

The data indicate a very close resemblance of both complexes in all major bond distances and angles within the standard deviation, and need no further discussion. As noted before,²¹ the Mo—P

Table 2. Comparison of selected bond lengths (Å) and bond angles (°) for $[C_5H_5Mo(CO)_3{P(C_6H_5)_3}]BF_4$ (VII) and $[C_5(CH_3)_5Mo(CO)_3{P(C_6H_5)_3}]BF_4 \cdot 0.5CH_3OH^{\alpha}$

	$[C_{5}H_{5}Mo(CO)_{3}{P(C_{6}H_{5})_{3}}]^{+}$	$[C_{5}(CH_{3})_{5}Mo(CO)_{3}{P(C_{6}H_{5})_{3}}]^{+}$
Mo-P(9)	2.5314(8)	2.562(2)
Mo-C(1)	2.300(3)	2.408(7)
Mo-C(2)	2.296(3)	2.333(8)
MoC(3)	2.325(3)	2.305(8)
MoC(4)	2.344(3)	2.292(7)
MoC(5)	2.343(3)	2.347(10)
Mo-C(6)	2.017(3)	1.991(11)
Mo-C(7)	2.007(4)	1.975(10)
Mo-C(8)	2.010(4)	1.995(10)
C(6)O(6)	1.130(4)	1.138(10)
C(7)-O(7)	1.135(4)	1.170(10)
C(8)-O(8)	1.135(4)	1.134(10)
P(9)—C(11)	1.833(3)	1.812(5)
P(9)—C(21)	1.831(3)	1.821(5)
P(9)—C(31)	1.818(3)	1.819(5)
P(9)	129.00(9)	122.5(3)
P(9)—Mo—C(7)	77.5(1)	76.4(2)
P(9)—Mo—C(8)	75.43(9)	77.5(2)
C(6)—Mo—C(7)	77.5(1)	76.9(4)
C(6)—Mo—C(8)	76.9(1)	74.4(4)
C(7)—Mo—C(8)	116.1(1)	121.1(4)
Mo-C(6)-O(6)	179.0(3)	176.5(8)
Mo-C(7)-O(7)	176.7(3)	176.9(9)
MoC(8)O(8)	179.2(3)	174.9(9)
Mo—P(9)—C(11)	113.0(1)	114.1(2)
Mo-P(9)-C(21)	116.0(1)	115.2(2)
Mo-P(9)-C(31)	113.3(1)	114.3(2)

^a Data from ref. 21 using the atom numbering from Fig. 3.



Fig. 3. ORTEP presentation of the cation $[C_5H_5Mo(CO)_3{P(C_6H_5)_3}]BF_4$ (VII) showing 50% probability ellipsoids.

bond is slightly longer than in the comparable neutral $C_5H_5Mo(CO)_2P(C_6H_5)_3$ complexes (2.48–2.52 Å)²² which may be attributed to the cationic nature of both complexes.

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