Generation and Trapping of a Superelectrophilic Terminal Fluorophosphinidene Complex

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Summary: Comparative DFT calculations on terminal phosphinidene complexes [MeP-Cr(CO)$_5$] and [FP-Cr(CO)$_5$] show a huge increase of the positive charge at P when replacing the methyl by the fluorine substituent (NBO charges +0.60 and +0.94). The electrophilic fluorination of the (3,4-dimethylphospholyl)pentacarbonylmolybdenum anion by Selectfluor gives a straightforward access to the corresponding 1-fluoro-3,4-dimethylphosphole molybdenum complex. This complex reacts as a conjugated diene with dimethyl acetylenedicarboxylate to give the corresponding 7-fluoro-7-phosphanorbornadiene complex. This bicyclic species is a precursor of [FP-Mo(CO)$_5$] at 120 °C in xylene, as shown by trapping reactions with diphenylacetylene and 2,3-dimethylbutadiene.

Introduction

The η^1-coordination of phosphinidenes to transition metals yields terminal complexes whose chemistry heavily depends on the nature of the coordinated metal. With low-valent metals at the right of the periodic table, phosphorus behaves as an electrophilic center, whereas, with high-valent metals at the left of the periodic table, phosphorus behaves as a nucleophilic center. Typical examples include [RP-M(CO)$_5$] (M = Cr, Mo, W) (unstable, electrophilic),[1,2] [RP-Ru(CO)$_2$Cp*]$^+$ (stable, electrophilic),[3] and [RP-Zr(PMe$_3$)Cp$_2$] (stable, nucleophilic).[4] This dichotomy has been studied in some depth from a theoretical standpoint.[5,6] Although, intuitively, the substituent at P might also play a significant role in the chemical reactivity of these complexes, this question has not received any attention until now. In the case of the widely used [RP-M(CO)$_5$] complexes, it was more precisely quite interesting to see whether it was possible to enhance the phosphorus electrophilicity that governs all of their chemistry. From this standpoint, the choice of the fluorine substituent was quite obvious. In this report, we compare [MeP-Cr(CO)$_5$] and [FP-Cr(CO)$_5$] from a theoretical standpoint. In so doing, we show that the fluorophosphinidene complex displays a much higher electrophilicity than its methyl analogue. Besides, we describe the generation and trapping of the molybdenum analogue [FP-Mo(CO)$_5$], thus opening the possibility to study the chemistry of these superelectrophilic species.

Results and Discussion

To evaluate the effect of the introduction of a fluorine substituent in [RP-M(CO)$_5$], we first decided to perform comparative DFT calculations[7] on [MeP-Cr(CO)$_5$] and [FP-Cr(CO)$_5$] using the B3LYP functional[8,9] with 6-31G(d) basis sets for all atoms except Cr (lanl2dz). Our results on [MeP-Cr(CO)$_5$] are close to those of Nguyen and co-workers on the same species.[10] The replacement of the methyl by the fluorine substituent induces some significant changes in the geometry of the complex. The R−P−Cr angle decreases from 112.5° (Me) to 109.4° (F). Similarly, the P−Cr bond is shortened from 2.270 Å (Me) to 2.207 Å (F). This does not necessarily mean that the strength of the P−Cr bond has increased since the out-of-phase P-Cr-*trans*-C(O) vibration is displaced at the same time toward lower frequencies (from 440.8 to 435.8 cm^{-1}). The absence of correlation between bond lengths and bond strengths has already been noticed in [R$_3$P-M(CO)$_5$] complexes.[11] Curiously the LUMO (essentially the phosphorus p_y orbital perpendicular to the Cr−P−R plane) is not affected by the replacement of Me by F, but the HOMO (essentially the in-plane lone pair at P) is lowered by 0.49 eV. Drastic changes are also observed on the NBO charges. The positive charge at P increases from 0.60 to 0.94 e. It is thus clear that [FP-Cr(CO)$_5$] will behave as a superelectrophile.

From a practical standpoint, building an appropriate precursor of [FP-M(CO)$_5$] is not trivial since the fluorine substituent is known to drastically enhance the stability of the rings whose thermal cycloreversion normally generates the phosphinidene species. This is especially true for the 7-phosphanorbornadiene system. A (7-fluoro-7-phosphanorbornadiene)pentacarbonyltungsten complex has been shown to be stable up to 160 °C.[12]

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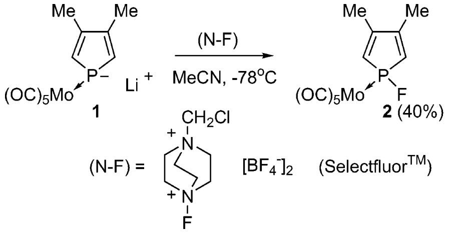
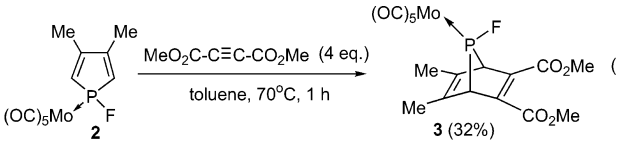
We reasoned that a stronger P−M bond is likely to induce a stronger stabilization of the phosphorus ligand. In the [R_3P-M(CO)$_5$] series, the P−M bond dissociation energies always vary in the order W−P > Cr−P > Mo−P.[11] For example, for R = Me, the computed data are as follows: W−P 43.8, Cr−P 41.2, and Mo−P 37.9 kcal mol^{-1}.[11] Since we were looking for a less stable 7-phosphanorbornadiene complex, it was thus tempting to investigate the synthesis and thermal splitting of a (7-fluoro-7-phosphanorbornadiene)pentacarbonylmolybdenum complex. Due to the higher reactivity of the Mo(CO)$_5$ group toward a strong chlorinating reagent such as SO_2Cl_2, it was difficult to transpose the previously described synthesis of the (1-fluoro-3,4-dimethylphosphole)pentacarbonyltungsten starting product, which implies a chlorination of the complexed phospholide, followed by a chlorine to fluorine exchange.[12] Our new, easier, and simpler approach involves the direct electrophilic fluorination of the (3,4-dimethylphospholyl)-pentacarbonylmolybdenum anion (**1**) by Selectfluor at low temperature (eq 1).[13]



(1)

The reaction is easily monitored by ^{31}P NMR spectroscopy. The ^{31}P resonance of the starting complexed anion (δ^{31}P(**1**) −35 ppm) is replaced by the resonance of the fluorophosphole complex (**2**), which appears as a doublet at 191.5 ppm in $CDCl_3$ ($^1J_{P-F}$ = 914.4 Hz). This fluoro complex tends to spontaneously dimerize to give a [4+2] dimer (1 h at 50 °C in toluene). This dimerization competes with the [4+2] cycloaddition with dimethyl acetylenedicarboxylate, which was carried out in dilute solution with a 4-fold excess of the acetylenic reagent (eq 2).



(2)

The cycloadduct **3** is characterized by the low-field shift of its ^{31}P resonance: δ^{31}P(**3**) 239, $^1J_{P-F}$ = 1016 Hz ($CDCl_3$). It is accompanied by ca. 10% of an isomer, **3a**, which likely corresponds to the cycloaddition of the CC triple bond on the other face of phosphole **2**: δ^{31}P(**3a**) 269, $^1J_{P-F}$ = 1031 Hz ($CDCl_3$). The mass spectrum (FAB) shows the molecular peak of **3** at *m*/*z* 511 (M + 1, ^{98}Mo) and the M − 5CO peak at *m*/*z* 370. A striking demonstration of the enhanced stability provided to the bicyclic structure by the fluorine substituent is the total absence of peaks corresponding to the terminal phosphinidene complex [FP-Mo(CO)$_5$] at *m*/*z* 288 (molecular peak) and 260 (M − CO, base peak), contrary to what happens with other 7-phosphanorbornadiene complexes.[14] The stereochemistry of **3** was established by an X-ray crystal structure analysis (Figure 1). As usual, the cycloaddition takes place on the least hindered side of the phosphole ring corresponding to the fluorine substituent. At 80.3°, the C(1)−P(1)−C(4) bridge angle is somewhat larger than that (79.0°) found in a more classical 7-phosphanorbornadiene complex.[14] The P−C bonds are also significantly shorter than in the normal case: 1.8605−1.8616(16) vs 1.877−1.878(3) Å.[14]

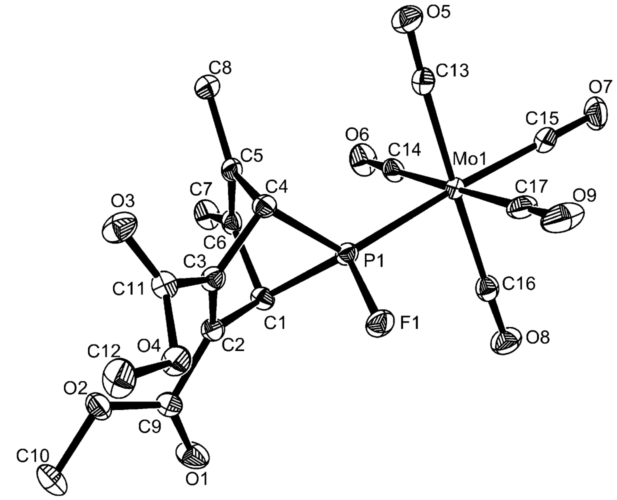
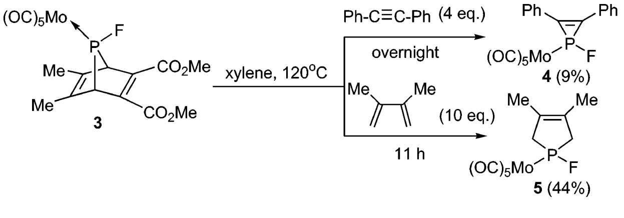


Figure 1. ORTEP drawing of one molecule of **3**. Ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): P(1)−Mo(1) 2.4521(5), P(1)−F(1) 1.5998(10), P(1)−C(1) 1.8605(17), P(1)−C(4) 1.8616(16); C(1)−P(1)−C(4) 80.29(7), F(1)−P(1)−C(1) 103.65(7), F(1)−P(1)−C(4) 104.23(6), F(1)−P(1)−Mo(1) 109.02(4).

Despite these negative indications, we decided to study the decomposition of **3** in the presence of trapping reagents. The first experiments were carried out with an excess of diphenylacetylene. At 120 °C overnight in xylene, the ^{31}P resonance of **3** disappears and is replaced by a new resonance at −16.7 ppm ($^1J_{P-F}$ = 1127.5 Hz). The product proved to be very sensitive to hydrolysis and even more difficult to purify than the other P−F compounds. The most significant clue to establish its structure was the exact mass as measured by FAB: found: 465.9326; calcd for $C_{19}H_{10}FMoO_5P$ (^{98}Mo): 465.930395. The huge upfield shift of the phosphorus resonance when compared to **2** and **3** was also a strong indication in favor of the three-membered ring structure. The recorded ^{31}P chemical shift is compatible with the data on free 1-fluorophosphirenes.[15] Thus the formulation of this product as a fluorophosphirene complex (**4**) is highly likely, but we have no X-ray crystal structure analysis to definitively prove it. Another reaction was thus performed with an excess of 2,3-dimethybutadiene. The reaction is complete after 11 h at 120 °C (eq 3).



(3)

The product of the reaction (**5**) shows a ^{31}P resonance at 217.2 ppm in C_6D_6 ($^1J_{P-F}$ = 852.3 Hz). Its phospholene structure was established by X-ray crystal structure analysis (Figure 2). The phosphanorbornadiene complex **3** is thus a genuine precursor of the fluorophosphinidene complex [FP-Mo(CO)$_5$].

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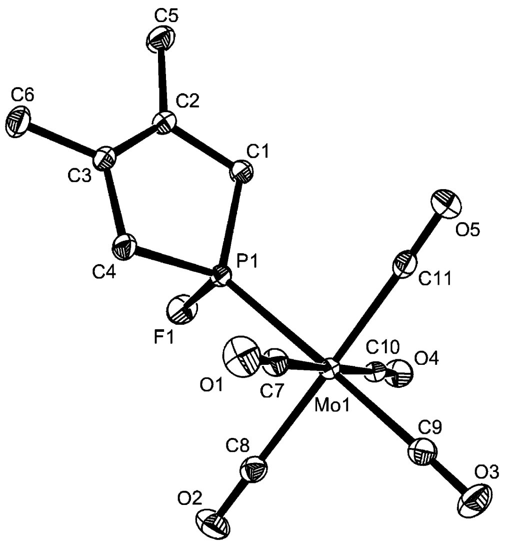

Figure 2. ORTEP drawing of one molecule of **5**. Ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): P(1)−Mo(1) 2.4456(5), P(1)−F(1) 1.5975(10), P(1)−C(1) 1.8201(15), P(1)−C(4) 1.8207(15); C(1)−P(1)−C(4) 93.91(7), F(1)−P(1)−C(1) 99.34(7), F(1)−P(1)−C(4) 99.38(7), F(1)−P(1)−Mo(1) 113.44(4).

Experimental Section

General Procedures. Reactions were performed under nitrogen using oven-dried glassware. Dry tetrahydrofuran was obtained by distillation from Na/benzophenone. Due to their high hydrolytic sensitivity, the products were purified by chromatography on Florisil. The modest isolated yields do not reflect the intrinsic yields of the reactions. Elemental analyses were precluded by the instability of the products. Nuclear magnetic resonance spectra were obtained on a Bruker Avance 3000 and Varian Inova spectrometer operating at 300.13 MHz for ^{1}H, 75.45 MHz for ^{13}C, and 121.496 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained on VG 7070 and Hewlett-Packard 5989A GC/Ms spectrometers. Selectfluor was bought from Aldrich and used as received.

(1-Fluoro-3,4-dimethylphosphole)pentacarbonylmolybdenum (2). To a THF solution (40 mL) of 3,4-dimethyl-1-phenylphosphole (3 g, 16×10^{-3} mol) was added an excess of lithium wire (with 1% of Na). The mixture was stirred overnight at RT. The excess of lithium was removed, and $AlCl_3$ (0.5 g) was added (45 min stirring), then ^{t}BuCl (0.4 mL, 30 min stirring). To the resulting solution was slowly added molybdenum hexacarbonyl (4.2 g, 16×10^{-3} mol) at 0 °C over 35 min. After 45 min, the solution was monitored by ^{31}P NMR and cooled at −70 °C. A solution of Selectfluor (4.2 g, 12×10^{-3} mol) in acetonitrile (70 mL) was added and the mixture stirred for 30 min at −70 °C, then warmed to RT. After evaporation of the solvents, the residue was extracted with pentane. The evaporation of pentane left yellow crystals of **2**. Yield: 2.3 g (40%). ^{31}P NMR ($CDCl_3$): δ 191.5 ($^{1}J_{P-F} = 914$ Hz). ^{1}H NMR ($CDCl_3$): δ 2.09 (d, 6H, $^{4}J_{H-P} = 2.7$ Hz, CH_3), 6.17 (d, 2H, $^{2}J_{H-P} = 39.2$ Hz, =CH). ^{13}C NMR ($CDCl_3$): δ 16.9 (d, $^{3}J_{C-P} = 11.5$ Hz, CH$_3$), 125.3 (dd, $^{1}J_{C-P} = 36.8$ Hz, $^{2}J_{C-F} = 10.3$ Hz, =CH), 151.0 (d, $^{2}J_{C-P} = 11.5$ Hz, Me-C=), 204.1 (d, $^{2}J_{C-P} = 10.3$ Hz, CO cis), 208.0 (d, $^{2}J_{C-P} = 26.5$ Hz, CO trans).

7-Fluoro-7-phosphanorbornadiene Pentacarbonylmolybdenum Complex (3). A mixture of fluorophosphole complex **2** (0.2 g, 5.5×10^{-4} mol) and dimethyl acetylenedicarboxylate (0.31 g, 2.2×10^{-3} mol) in toluene (2 mL) was heated at 70 °C for 1 h. After evaporation of the solvent, the residue was purified by chromatography on Florisil with hexane/dichloromethane (1:1) as the eluent. Yield: 0.089 g (32%) of maroon crystals of **3**. ^{31}P NMR ($CDCl_3$): δ 239 ($^{1}J_{P-F} = 1016$ Hz). ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 6H, CH_3), 3.87 (s, 6H, OCH_3), 3.90 (pseudo-t, 2H, $^{2}J_{H-P} = {}^{3}J_{H-F} = 12.3$ Hz, P-CH). ^{13}C NMR ($CDCl_3$): δ 16.1 (s, CH$_3$), 52.82 (s, O-CH$_3$), 62.17 (pseudo-t, $^{1}J_{C-P} = {}^{2}J_{C-F} = 8.1$ Hz, C-P), 134.28 (d, $^{2}J_{C-P} = 20.7$ Hz, =CMe), 141.96 (s, =C-CO$_2$Me), 164.72 (s, COO), 203.39 (*cis*-CO). EIMS (^{98}Mo): *m/z*: 510 (M^{+}, 30%), 426 (M − 3CO, 58%), 370 (M − 3CO, 100%).

(1-Fluoro-2,3-diphenylphosphirene)pentacarbonylmolybdenum (4). Precursor **3** (0.45 g, 9×10^{-4} mol) and tolan (0.64 g, 3.3×10^{-3} mol) in xylene (4 mL) were heated overnight at 120 °C in a Schlenk tube. After evaporation of the solvent, the residue was chromatographed on Florisil with hexane as the eluent. Yield of white crystals: 0.037 g, 9%. ^{31}P NMR ($CDCl_3$): δ −16.7 ($^{1}J_{P-F} = 1127$ Hz). ^{13}C NMR ($CDCl_3$): δ 149.4 (pseudo-t, $^{1}J_{C-P} = {}^{2}J_{C-F} = 19$ Hz, =CPh), 204.2 (d, $^{2}J_{C-P} = 12.7$ Hz, CO cis), 208.6 (d, $^{2}J_{C-P} = 44.6$ Hz, CO trans). Exact mass: calcd for $C_{19}H_{10}FMoO_5P$ (^{98}Mo) 465.930395; found (FAB) 465.9326.

(1-Fluoro-3,4-dimethylphosphol-3-ene)pentacarbonylmolybdenum (5). Precursor **3** (0.32 g, 6.3×10^{-4} mol) and 2,3-dimethylbutadiene (0.52 g, 6.3×10^{-3} mol) in xylene (8 mL) were heated for 11 h at 120 °C in a Schlenk tube. After evaporation of the solvent, the residue was chromatographed on Florisil with hexane/dichloromethane (4:1) as the eluent. Yield of white crystals: 0.1 g, 44%. ^{31}P NMR ($CDCl_3$): δ 217 ($^{1}J_{P-F} = 857$ Hz). ^{1}H NMR (C_6D_6): δ 1.22 (s, 6H, Me), 2.33 (m, 4H, CH$_2$). ^{13}C NMR (C_6D_6): δ 15.7 (d, $^{3}J_{C-P} = 8.1$ Hz, CH$_3$), 49.8 (dd, $^{1}J_{C-P} = 16.1$ Hz, $^{2}J_{C-F} = 13.8$ Hz, P-CH$_2$), 128.3 (s, C=C), 204.9 (d, $^{2}J_{C-P} = 10.3$ Hz, CO cis), 209.1 (d, $^{2}J_{C-P} = 28.8$ Hz, CO trans).

X-ray Structure Characterizations of 3 and 5. Measurements were carried out using a low-temperature device at $T = 100(2)$ K on a Bruker X8 APEX KAPPA-CCD X-ray diffractometer system[16] using Mo radiation ($\lambda = 0.71073$ Å). The automated strategy determination program COSMO[17] was used to find diffraction experiments on the basis of phi and omega scans. Frames were integrated using the Bruker SAINT version 7.06A software[18] and using a narrow-frame integration algorithm. The integrated frames yielded the following.

For $C_{17}H_{14}FO_9PMo$ (**3**) a total of 18 350 reflections were collected at a maximum 2θ angle of = 57.22° (4888 independent reflections, $R_{int} = 0.0202$, $R_{sig} = 0.0207$, completeness = 92.8%) and 4327 (88.52%) reflections were found greater than 2σ(I). Space group $P2(1)/c$. The unit cell parameters were $a = 7.8918(6)$ Å, $b = 32.555(3)$ Å, $c = 8.3793(7)$ Å, $\alpha = 90.0°$, $\beta = 107.2600(10)°$, $\gamma = 90.0°$, $V = 2055.8(3)$ Å^3, $Z = 4$, calculated density $D_c = 1.642$ Mg/m^3.

For $C_{11}H_{10}FO_5PMo$ (**5**) a total of 10 783 reflections were collected at a maximum 2θ angle of 56.56° (3382 independent reflections, $R_{int} = 0.0214$, $R_{sig} = 0.0236$, completeness = 98.0%) and 3000 (88.70%) reflections were found greater than 2σ(I). Space group $P2(1)/n$. The unit cell parameters were $a = 11.0324(17)$ Å, $b = 6.8608(11)$ Å, $c = 18.504(3)$ Å $\alpha = 90.0°$, $\beta = 97.287(2)°$, $\gamma = 90.0°$, $V = 1252.9(2)$ Å^3, $Z = 4$, calculated density $D_c = 1.760$ Mg/m^3.

Absorption corrections were applied for all data using the SADABS program included in the SAINTPLUS software package.[18] Direct methods using the Sir92 program[19] were used for resolution. Direct methods of phase determination followed by a subsequent difference Fourier map led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit. With subsequent isotropic refinement and some Fourier differences synthesis, all non-hydrogen atoms were identi-

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(16) *APEX 2* version 1.0-22; Bruker AXS Inc.: Madison, WI, 2004.

(17) *COSMO NT* version 1.40; Bruker AXS Inc.: Madison, WI.

(18) *SAINTPLUS Software Reference Manual*, Version 6.02A; Bruker Analytical X-Ray System, Inc.: Madison, WI, 1997−1998.

(19) *SIR92*−A program for crystal structure solution. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

fied, and atomic coordinates and isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2, using SHELXTL software.[20] Hydrogen atoms were included in the refinement in calculated positions, riding on the carbons atoms. Isotropic thermal parameters of H atoms were fixed 20% and 50% higher than Csp^2 and Csp^3 atoms, respectively, to which they were connected, and torsion angles for methyl groups were refined. The refinement converged at $R1 = 0.0231$, $wR2 = 0.0512$, with intensity $I > 2\sigma(I)$, and largest peak/hole in the final difference map were found to be 0.441 and -0.274 e $Å^{-3}$ for $C_{17}H_{14}FO_9PMo$. $R1 = 0.0180$, $wR2 = 0.0432$, with intensity $I > 2\sigma(I)$, and largest peak/hole in the final difference map were found to be 0.411 and -0.335 e $Å^{-3}$ for **6**. Drawings of molecules were achieved using ORTEP32.[21]

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Supporting Information Available: X-ray crystal structure analysis of compounds **2** and **6**. Copies of the ^1H and ^{13}C NMR spectra of **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) *SHELXTL Software Reference Manual*, Version 6.10; Bruker Analytical X-Ray System, Inc.: Madison, WI, 2000.

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