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Generation and Trapping of a Terminal Chlorophosphinidene Complex

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A huge amount of work has been devoted recently to the chemistry of terminal phosphinidene complexes.[1] As do carbene complexes, they exist in two varieties, the nucleophilic type displaying a phospha-Wittig reactivity, and the electrophilic type displaying a reactivity closely similar to that of singlet carbenes. Within this last category, the most studied and useful species are the transient pentacarbonyl complexes of group VI transition metals. Among them, the halophosphinidene complexes are conspicuous by their absence. This is all the more frustrating since they would combine a higher electrophilicity than the aryl or alkyl species with the additional synthetic potential of the P−X bond. Our preliminary attempts with fluorophosphinidene complexes yielded mixed results.[2] We have been able to generate [FP-Mo(CO)$_5$] at 120 °C in xylene, but the conditions were too drastic to get satisfactory trapping reactions. We thus decided to reinvestigate this problem in more depth.

Before starting our experiments, we performed comparative DFT calculations[3] on [FP-Cr(CO)$_5$], [ClP-Cr(CO)$_5$], and [MeP-Cr(CO)$_5$] at the B3LYP/6-31G(d)-lanl2dz(Cr) level.[4] The results were somewhat surprising. The NBO charge at P appears to be lower for Cl (+0.55e) than for Me (+0.60e) and F (+0.94e). This means that there is a strong interaction between the chlorine lone pairs and the vacancy at phosphorus in [ClP-Cr(CO)$_5$], as confirmed by the shapes of the HOMO and LUMO (Figure 1).

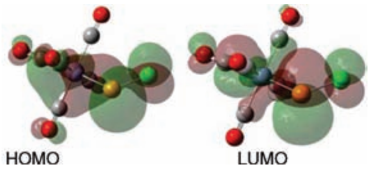


Figure 1. HOMO and LUMO of [Cl-P-Cr(CO)$_5$].

The in-plane σ lone pair at P (HOMO) is stabilized by the interaction with chlorine, whereas the empty p_z orbital at P (LUMO) is destabilized. This destabilization is weak because the P−Cl bond is long (2.107 Å). In the case of fluorine, the destabilization is much stronger because the P−F bond is short (1.632 Å). The result is that the levels of the HOMOs and the LUMOs are differently perturbed in [Cl-P-Cr(CO)$_5$] and [F-P-Cr(CO)$_5$] when compared to [Me-P-Cr(CO)$_5$], as shown in Figure 2. The unexpected prediction of these computations is that the chlorophosphinidene complex would behave as the most electrophilic of the three species, since its LUMO is significantly lower in energy than the two others.

Of the four available methods in use for the generation of phosphinidene complexes, both the phosphepine[5] and the azaphosphirene[6] routes are difficult to transpose for the synthesis of chlorophosphinidene complexes. The phosphirane[7] route is also useless because 1-chlorophosphirane complexes[8] are known to be highly stabilized by chlorine substitution[9] and cannot generate [Cl-P-M(CO)$_5$] under acceptable conditions. We are left with our original 7-phosphanorbornadiene route.[10] In this case, we must start from the 1-chloro-3,4-dimethylphosphole complex (**1**). This complex is known[11] but delicate to prepare due to the use of SO_2Cl_2. Thus, we first decided to modify its synthesis. The new method is depicted in eq 1.

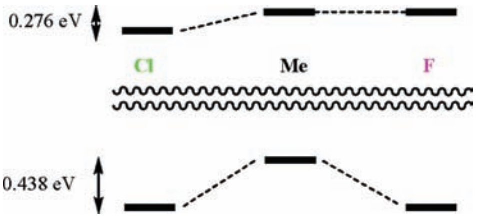
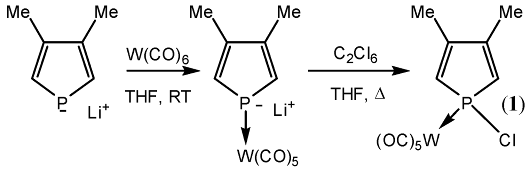


Figure 2. HOMO and LUMO levels of [R-P-Cr(CO)$_5$], (R = Cl, Me, F).



(1)

As an additional characterization, we have recorded its ^{13}C NMR spectrum[12] and its X-ray crystal structure analysis (Figure 3).

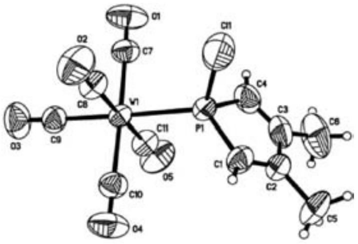


Figure 3. X-ray crystal structure of chlorophosphole (**1**). Main bond lengths (Å) and angles (deg): P1−W1 2.4516(8), P1−Cl1 2.0546(13), P1−C1 1.772(3), P1−C4 1.783(4), C1−C2 1.331(5), C2−C3 1.476(5), C3−C4 1.332(5); C1−P1−Cl1 101.66(13), C4−P1−Cl1 103.85(15), C1−P1−C4 91.24(17), C1−P1−W1 123.22(12), C4−P1−W1 118.84(13), Cl1−P1−W1 114.13(5).

The strong alternation between the single and double carbon−carbon bonds suggests some antiaromaticity within the ring as expected.

Our earlier investigation of the reaction of complex **1** with dimethyl acetylenedicarboxylate (DMAD) was completely negative.[11] Nevertheless, we decided to carefully monitor this same reaction in toluene by ^{31}P NMR. We discovered that, at 60 °C, the reaction proceeds slowly to give the expected 7-phosphanorbornadiene complex **2** with its characteristic low-field shift: δ ^{31}P(**2**) 188.2 ppm ($^1J_{PW}$ = 271 Hz). The peak reaches a maximum after

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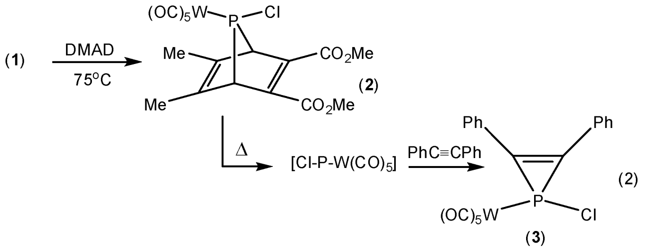
ca. 11−12 h, but the decomposition starts before all of the starting chlorophosphole **1** has been consumed. Attempted purification of **2** by chromatography completely failed. We repeated the same experiment at 75 °C in the presence of diphenylacetylene. After 5−6 h, a complete conversion of **1** into the known 1-chlorophosphirene complex **3**[13] was observed (δ ^{31}P(**3**) −109.2 ppm, $^1J_{PW}$ = 323 Hz) (eq 2).



This last experiment convincingly demonstrated that the system **1** + DMAD can be used as a precursor for [Cl-P-W(CO)$_5$]. A similar experiment was then carried out with cyclohexene replacing diphenylacetylene. The resulting phosphirane **4**[14] was characterized by X-ray crystal structure analysis (Figure 4).

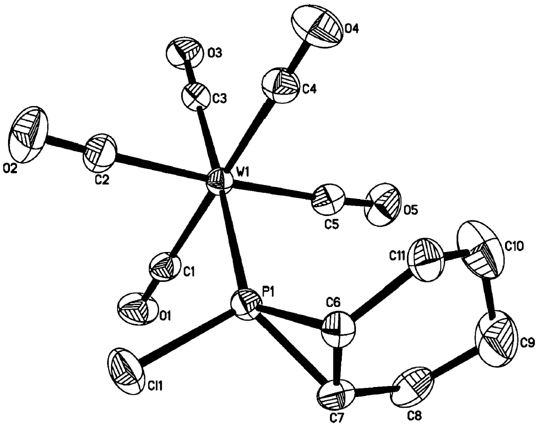
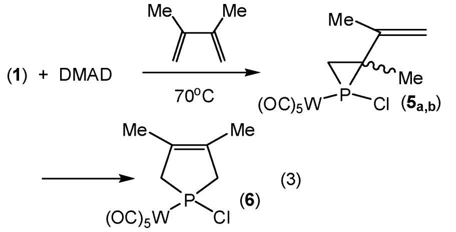


Figure 4. X-ray crystal structure of chlorophosphirane (**4**). Main bond lengths (Å) and angles (deg): P1−W1 2.4788(10), P1−Cl1 2.0534(14), P1−C6 1.813(4), P1−C7 1.825(4), C6−C7 1.536(5); C6−P1−C7 49.93(17), C6−P1−Cl1 102.14(13), C7−P1−Cl1 103.45(14), C6−P1−W1 134.15(12), C7−P1−W1 133.63(13), Cl1−P1−W1 115.97(5).

Whereas the reaction of [PhP-W(CO)$_5$] with cyclohexene gives the expected nonseparable mixture of isomers with the cyclohexane ring *cis* or *trans* to tungsten,[15] it is striking to find exclusively the more hindered *cis* isomer was obtained.

If the trapping reagent is also able to react with DMAD, it might prove difficult to trap [ClP-W(CO)$_5$] whose concentration in the reaction medium is very low. In fact, this is not the case. The reaction of **1** + DMAD with 2,3-dimethylbutadiene was carried out at 70 °C for 16 h in toluene. We detected the formation of the two expected isomeric chlorophosphiranes **5$_{a,b}$** (δ ^{31}P −64.5 and −58.8 ppm) and their rearrangement into the chlorophospholene **6**[16] (eq 3)



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Supporting Information Available: Complete ref 3. Complete experimental section. X-ray crystal structure analysis of compounds **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Purified by flash chromatography on silica gel with hexane as the eluent, overall yield *ca.* 48%. ^{31}P NMR (CD_2Cl_2): δ 74.0 ($^1J_{PW}$ = 259 Hz); ^{13}C NMR (CD_2Cl_2): δ 17.04 (d, $^3J_{CP}$ = 12 Hz, Me), 130.14 (d, $^1J_{CP}$ = 36 Hz, =CH−P), 151.59 (d, $^2J_{CP}$ = 12 Hz, Me−C=), 195.48 (d, $^2J_{CP}$ = 8 Hz, *cis*-CO), 198.94 (d, $^2J_{CP}$ = 28 Hz, *trans*-CO).

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(14) Purified by flash chromatography on silica gel with hexane as the eluent, overall yield *ca.* 30%. ^{31}P NMR (CD_2Cl_2): δ−64.0 ($^1J_{PW}$ = 298 Hz); ^{13}C NMR (CD_2Cl_2): δ 21.64 (d, J_{CP} = 3.6 Hz, CH_2), 22.23 (d, J_{CP} = 2.4 Hz, CH_2), 28.49 (d, $^1J_{CP}$ = 21.9 Hz, CH−P), 195.45 (d, J_{CP} = 8.5 Hz, *cis*-CO), 198.05 (d, J_{CP} = 41.3 Hz, *trans*-CO).

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(16) The crude product was extracted with pentane at−10°C and then purified by chromatography at 0 °C with CH_2Cl_2 (overall yield 18%). ^{31}P NMR (toluene): δ 103.6 ($^1J_{PW}$ = 264 Hz); ^{1}H NMR (CD_2Cl_2): δ 1.77 (s, Me), 2.90 (ABX, CH_2−P); ^{13}C NMR (CD_2Cl_2): δ 16.33 (d, $^3J_{CP}$ = 7.4 Hz, Me), 50.75 (d, $^1J_{CP}$ = 24.6 Hz, CH_2−P), 129.67 (s, Me−C=), 196.74 (d, $^2J_{CP}$ = 7.4 Hz, *cis*-CO), 200.34 (d, $^2J_{CP}$ = 23.4 Hz, *trans*-CO). The free 1-chloro-3,4-dimethylphosphol-3-ene has been described: Vizel, A. O.; Krupnov, V. K.; Arbuzov, B. A.; Fadeeva, L. M. *Zh. Obshch. Khim.* **1973**, *43*, 2137.

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