Notes

Electrochemical Decomplexation of Phosphine-Pentacarbonyltungsten Complexes: The Phosphole Case

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Summary: Electrochemical reduction of phosphole P-W-(CO)$_5$ complexes affords the free phospholes in good yields. This technique allows the decomplexation of a 2-ethoxy-4-keto-4,5-dihydrophosphole, which has been characterized by X-ray crystal structure analysis of its P-sulfide.

Introduction

The transient electrophilic terminal phosphinidene complexes [R-P-M(CO)$_5$] (M = Cr, Mo, W) combine easy access, large range of substituents, and an impressive array of reactions with organic or organometallic molecules.[1,2] The original access through thermal decomposition of the appropriate 7-phosphanorbornadiene complexes is still the major route to these carbene-like species. As such, they already constitute a powerful tool for making new organophosphorus structures. These structures are obtained as their P-M(CO)$_5$ complexes, and hence, to be fully effective, this chemistry needs to be coupled to efficient decomplexation techniques. Indeed, while the complexing groups are useful for tuning the electrophilicity and the lifetime of the phosphinidene moiety and increasing the stability and tractability of the reaction products, they must be removed if useful ligands or biologically active molecules are the final targets of the synthetic work.

In practice, the most effective complexing group is the pentacarbonyltungsten unit. As might be expected, this is also the one that gives the strongest bond to the P atom. Presently, only three decomplexation techniques have been applied to its removal with some success. The oldest method involves an oxidation of W(0) to W(II) by iodine, which weakens the P−W bond, followed by a displacement of the phosphorus ligand by 1-methyl-1*H*-imidazole.[3,4] In a variant of this first technique, pyridinium tribromide is used as the halogenation reagent and 2,2′-bipyridine for the displacement.[5]

Another method relies on the displacement of the P ligand by a chelating bidentate diphosphine such as $Ph_2PCH_2CH_2PPh_2$ and, of course, can only be applied to the decomplexation of monodentate ligands. Reported examples include bifunctional phospholes[6] and 1-chlorophosphirenes.[7]

The third group of methods involves oxidative conditions. Trimethylamine oxide has been shown to be the reagent of choice for the conversion of [P-W(CO)$_5$] complexes into the corresponding phosphoryl compounds.[8]

As might be guessed, all these methods suffer from severe limitations and only a restricted number of products resulting from this phosphinidene chemistry have been isolated as free species. Hereafter, we propose a completely different decomplexation technique, which works under reductive conditions and thus nicely supplements the earlier methods.

Results and Discussion

We decided to investigate the electrochemical properties of [R_3P-W(CO)$_5$] complexes by cyclic voltammetry (CV) using a series of phosphole complexes as the model compounds. In all cases on the CV curves, only one two-electron irreversible reduction wave was observed. A typical curve is shown in Figure 1. The potentials and peak currents are presented in Table 1. As can be seen from the data, all these potentials are in the range of the reduction potential of [W(CO)$_6$] under the same

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(1) Review: Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938.

(2) Review: Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, *4*, 1127.

(3) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 45.

(4) For a recent example, see: van Eis, M. J.; Zappey, H.; de Kanter, F. J. J.; de Wolf, W. H.; Lammertsma, K.; Bickelhaupt, F. *J. Am. Chem. Soc.* **2000**, *122*, 3386.

(5) Marinetti, A.; Mathey, F.; Fischer, J. *J. Am. Chem. Soc.* **1985**, *107*, 5001.

(6) Espinosa-Ferao, A.; Deschamps, B.; Mathey, F. *Bull. Soc. Chim. Fr.* **1993**, *130*, 695.

(7) Deschamps, B.; Mathey, F. *Synthesis* **1995**, 941.

(8) Tran Huy, N. H.; Mathey, F. *J. Org. Chem.* **2000**, *65*, 652.

10.1021/om030671g CCC: $27.50

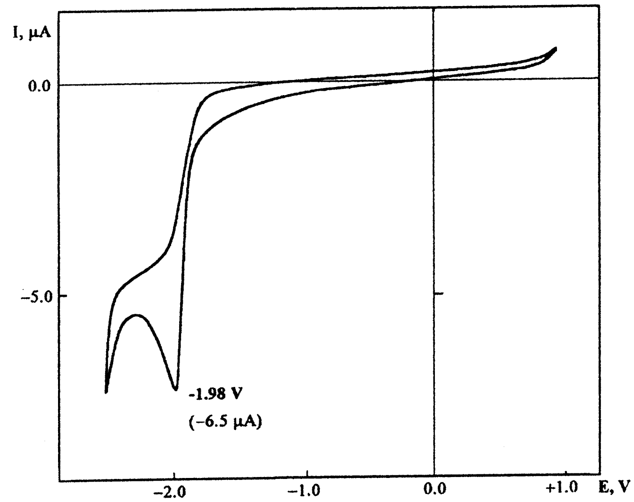
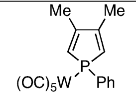
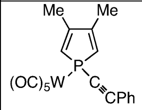
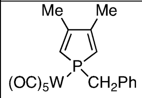
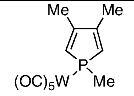
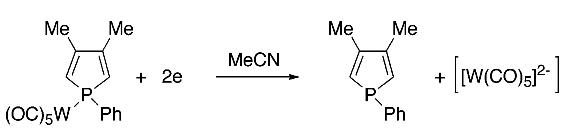


Figure 1. CV of 1-phenyl-3,4-dimethylphospholepentacarbonyltungsten complex.

Table 1. Reduction Potentials and Peak Currents from the CV Curves of Phosphole-Pentacarbonyltungsten Complexes (5×10^{-3} M acetonitrile solution, scan rate 100 mV s^{-1})

Phosphole complex	$\delta^{31}P$ ppm	$^{1}J_{P-W}$ Hz	E_p^{red} V	I_p^{red} μA
	9.7	207.4	-1.98	-6.5
	-25.3	212.3	-1.91	-6.0
	17.6	205.1	-2.16	-5.2
	-7.6	206.0	-2.08	-6.5

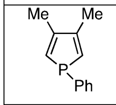
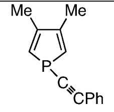
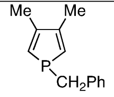
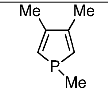
electrochemical conditions ($E_p^{red} = -2.19$ V, $I_p^{red} = -8.1$ μA). Moreover, two electrons are transferred at these potentials. To determine the evolution of the initially formed dianionic species, we decided to repeat these experiments on a preparative scale. Monitoring of the solution by ^{31}P NMR spectroscopy showed the complete disappearance of the resonance for the 1-phenyl-3,4-dimethylphosphole P-W(CO)$_5$ complex at +9.7 ppm and the appearance of a single P-containing product at −0.8 ppm. This product was isolated by column chromatography in 86% yield and identified as the free phosphole. Thus the overall electrochemical reduction scheme corresponds to eq 1.



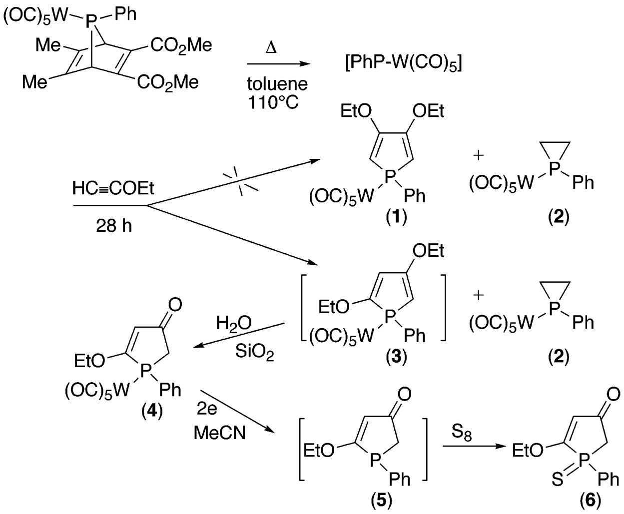
(1)

The presence of tungsten was detected in the anodic compartment of the electrochemical cell by the intense blue color of its oxidation products. This allows a useful preliminary separation of tungten-containing species from the desired free phosphorus heterocycle. Similar reductive electrochemical decomplexations were carried out with a series of phosphole pentacarbonyltungsten complexes (Table 2). As can be seen, the reaction is quite general and no problem arises from the electrochemical reduction of the free phospholes, which occurs at more negative potentials than the reduction of the corresponding complexes.

Table 2. Electrochemical Properties of Free Phospholes (5×10^{-3} M acetonitrile solution, scan rate 100 MV s^{-1}) and Decomplexation Yields of Phosphole Complexes (* conversion as measured by integration of the ^{31}P NMR peaks)

Free phosphole	$\delta^{31}P$ ppm (CH_3CN)	Decomplexation yields %	E_p^{red} V	I_p^{red} μA
	-0.8	86.4 (100*)	-2.54	-5.5
	-41.8	68*	-2.38	-4.3
	10.5	70*		
	-17.6	96*		

Scheme 1



We were eager to apply this new and mild electrochemical decomplexation technique to an original case. For that purpose, we decided to repeat a former experiment where the reaction of an excess of ethoxyacetylene with the transient phosphinidene complex [PhP-W(CO)$_5$] led to a variable mixture of the symmetrical 3,4-bis(ethoxy)phosphole complex **1** (δ ^{31}P −9.5 ppm in $CDCl_3$) together with the 1-phenylphosphirane complex **2** (δ ^{31}P −190.1 ppm in $CDCl_3$), whose proportion increased with the temperature (Scheme 1).[9] The reaction was carried out at 110 °C for 28 h. To our surprise, we were unable to get **1**. Instead, a mixture of **2** (δ ^{31}P −188.2 ppm in

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[9] Tran Huy, N. H.; Mathey, F. *Phosphorus Sulfur Silicon* **1990**, *47*, 477.

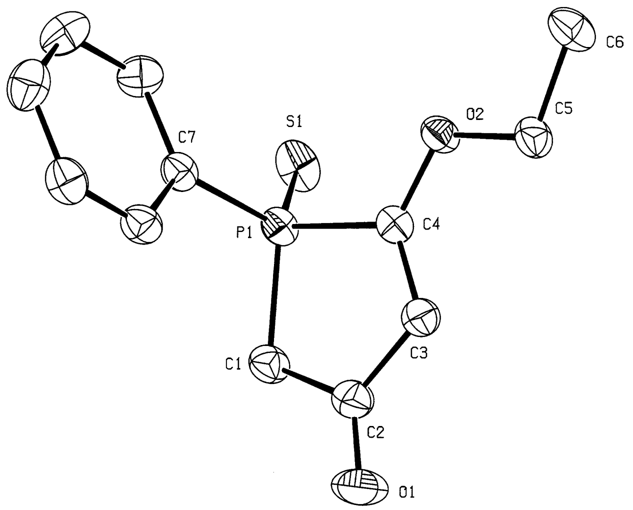

Figure 2. ORTEP drawing of one molecule of **6**. Thermal ellipsoids enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): P(1)−S(1) 1.9392(5), P(1)−C(1) 1.817(1), P(1)−C(4) 1.831(1), P(1)−C(7) 1.804(1), O(1)−C(2) 1.219(2), O(2)−C(4) 1.335(2), O(2)−C(5) 1.458(2), C(1)−C(2) 1.513(2), C(2)−C(3) 1.461(2), C(3)−C(4) 1.348(2); C(7)−P(1)−C(1) 108.06(6), C(7)−P(1)−C(4) 105.82(6), C(1)−P(1)−C(4) 92.07(6), C(7)−P(1)−S(1) 115.47(4), C(1)−P(1)−S(1) 118.31(5), C(4)−P(1)−S(1) 114.21(4), C(4)−O(2)−C(5) 115.4(1), C(2)−C(1)−P(1) 106.8(1), O(1)−C(2)−C(3) 123.9(1), O(1)−C(2)−C(1) 122.1(1), C(3)−C(2)−C(1) 113.9(1), C(4)−C(3)−C(2) 113.9(1), O(2)−C(4)−C(3) 129.2(1), O(2)−C(4)−P(1) 117.8(1), C(3)−C(4)−P(1) 113.1(1).

toluene) and a new product (**3**) (δ ^{31}P +11.8 ppm in toluene) was formed. During the chromatographic work-up, **3** hydrolyzed to give a new more stable product (**4**) (δ ^{31}P +0.03 ppm in $CDCl_3$) (Scheme 1).

The identification of **4** mainly relied on ^{13}C NMR spectroscopy and mass spectrometry. At *m/z* 544, the highest mass corresponds to the formulation. The ^{13}C spectrum in $CDCl_3$ shows a P−CH_2 resonance at 43.57 ($^{1}J_{C-P}$ = 27 Hz), a OCH_2 at 70.38 ($^{3}J_{C-P}$ = 5.2 Hz), a =CH at 111.55 ($^{2}J_{C-P}$ = 12 Hz), a (Ph)C−P at 132.77 ($^{1}J_{C-P}$ = 36.7 Hz), a (EtO)C−P at 186.87 ($^{1}J_{C-P}$ = 48 Hz), and carbonyls at 195.05 (d, $^{2}J_{C-P}$ = 6.8 Hz, *cis*-WCO), 197.27 (s, cyclic CO), and 198.46 (d, $^{2}J_{C-P}$ = 23.3 Hz, *trans*-WCO). We have no obvious explanation of why the insertion of the second molecule of alkyne into the initially formed phosphirene gave the symmetrical product **1** in our former experiments and the unsymmetrical product **3** in the present case, although the formation of **3** appears to be more logical from an electronic standpoint.

Anyhow, we applied the electrochemical decomplexation technique to complex **4**. Only one major irreversible reduction wave was observed ($E_p^{red} = -2.04$ V, $I_p^{red} = -5.6$ μA). Once again, the process corresponds to the transfer of two electrons. Monitoring the reaction mixture by ^{31}P NMR spectroscopy showed the formation of the decomplexation product **5** at −31.5 ppm. The product was reacted in situ with sulfur to give in 63% overall yield from **4** the stable sulfide **6**, which was fully characterized by X-ray crystal structure analysis (Figure 2). This successful decomplexation shows that this electrochemical technique is compatible with carbonyl and vinyl ether functionalities.

Finally, numerous electrochemical studies of $[M(CO)_n(PR_3)_{6-n}]$ complexes (M = Cr, Mo, W) have been described in the literature,[10] but as far as we know, they were all directed toward the characterization of the oxidation products, inter alia the 17e cationic species. From another standpoint, Kochi and others have studied electrochemical reductions of several 18-electron carbonyl complexes that dissociate a CO ligand upon electron transfer.[11]

Experimental Section

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 for ^{1}H, 75.47 for ^{13}C, and 121.50 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (^{1}H and ^{13}C) and external 85% aqueous H_3PO_4(^{31}P). Mass spectra were obtained at 70 eV with an HP 5989B spectrometer by the direct inlet method. All electrochemical experiments were carried out under a dry argon atmosphere. Acetonitrile was purified by distillation over P_4O_{10}. Supporting electrolyte Bu_4NBF_4 was recrystallized from ethyl acetate, melted, and dried in a vacuum. Cyclic voltammograms were recorded in CH_3CN in the presence of Bu_4NBF_4 (0.3 M) on a gold electrode (working surface 0.2 mm^2) in a thermostatically controlled three-electrode electrochemical cell (substrate concentration 5×10^{-3} M). Saturated calomel was used as the reference electrode. Platinum wire was used as an auxiliary electrode. Curve recording was performed at constant potential scan rate (100 mV s^{-1}). Preparative electrochemical reductions were performed in a preparative electrochemical cell with a separation of the anodic and cathodic compartments. A carbon-glass electrode (working surface 60 cm^2) was used as the working electrode. The electrolyses were carried out at room temperature in galvanostatic regime.

Electrochemical Decomplexation of (1-Phenyl-3,4-dimethylphosphole)pentacarbonyltungsten. (1-Phenyl-3,4-dimethylphosphole)pentacarbonyltungsten (0.1 g, 0.2×10^{-3} mol) was dissolved in acetonitrile (20 mL) containing Bu_4NBF_4 (0.3 M). Then a constant current of 10.72 mA was passed through the solution for 1 h. Complete conversion of the complex into the corresponding free phosphole was observed by ^{31}P NMR spectroscopy. The product was purified by chromatography on silica gel using hexane/dichloromethane, 9:1, as the eluent. The yield of isolated product was 84%.

Synthesis of Complex 4. A solution of 2,3-dimethyl-5,6-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene complex[3] (1.0 g, 1.53×10^{-3} mol) and 1 mL of a 40% solution of ethoxyacetylene in hexane (ca. 4×10^{-3} mol) was heated at 110 °C for 24 h in toluene (10 mL). After evaporation, the residue was chromatographed on silica gel, with hexane/diethyl ether (1:9) as the eluent: 0.28 g of **4** was isolated as a slightly yellow powder (yield 34%).

Electrochemical Decomplexation of (1-Phenyl-2-ethoxy-4-keto-4,5-dihydrophosphole)pentacarbonyltungsten (4). (1-Phenyl-2-ethoxy-4-keto-4,5-dihydrophosphole)pentacarbonyltungsten (**4**) (0.2 g, 0.37×10^{-3} mol) was dissolved in acetonitrile (20 mL) containing Bu_4NBF_4 (0.3 M). A constant current of 10 mA was passed through the solution for 2 h. Then sulfur (0.3 g) was added to the solution. After

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[10] See for example: Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617. Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 274. Bond, A. M.; Darensbourg, D. J.; Mocellin, E.; Stewart, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 6827. Bagchi, R. N.; Bond, A. M.; Brain, G.; Colton, R.; Henderson, T. L. E.; Kevekordes, J. E. *Organometallics* **1984**, *3*, 4.

[11] See for example: Ohst, H. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2897. Hershberger, J. W.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1982**, 213. Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351.

stirring for 45 min, the solvent was evaporated under vacuum. The product **6** was purified by chromatography on silica gel using hexane/ether, 9:1, as the eluent. The yield of isolated product was 63% (59 mg). ^{31}P NMR (CDCl$_3$): δ 35.6. ^{1}H NMR (CDCl$_3$): δ 1.37 (t, 3H, $J = 7.0$ Hz, CH$_3$), 3.17 (m, 2H, P$-$CH$_2$), 4.13 (q, 2H, O$-$CH$_2$), 6.04 (d, 1H, $J = 31.2$ Hz, CH$=$), 7.25$-$7.59 (m, 3H, Ph), 7.79$-$7.87 (m, 2H, Ph). ^{13}C NMR (CDCl$_3$): δ 14.24 (s, CH$_3$), 44.55 (d, $^1J_{\mathrm{C-P}} = 57.6$ Hz, P$-$CH$_2$), 70.38 (d, $^3J_{\mathrm{C-P}} = 7.1$ Hz, O$-$CH$_2$), 114.92 (d, $^2J_{\mathrm{C-P}} = 18.1$ Hz, $=$CH), 128.16 (d, $^1J_{\mathrm{C-P}} = 80.5$ Hz, P$-$C(Ph)), 180.12 (d, $^1J_{\mathrm{C-P}}$ ca. 81 Hz, P$-$C(OEt)), 193.68 (d, $^2J_{\mathrm{C-P}} = 7.7$ Hz, C$=$O). MS (EI): *m*/*z* (ion, relative abundance) 252 (M$^+$, 19), 251 (100).

Crystallographic Data for 6. $M = 252.25$ g/mol; monoclinic; space group $P2_1/n$; $a = 14.127(1)$ Å, $b = 6.204(1)$ Å, $c = 14.761(1)$ Å, $\beta = 108.001(1)°$, $V = 1230.4(2)$ Å^3; $Z = 4$; $D = 1.362$ g cm^{-3}; $\mu = 0.375$ cm^{-1}; $F(000) = 528$. Crystal dimensions 0.20 × 0.16 × 0.10 mm. Total reflections collected 5896 and 2894 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.087; $R(I > 2\sigma(I)) = 0.0352$, wR2 = 0.1029(all data); maximum/minimum residual density 0.305(0.052)/$-$0.360(0.052) e Å^{-3}. Data were collected on a KappaCCD diffractometer at 150.0(1) K with Mo Kα radiation ($\lambda = 0.71073$ Å). Full details of the crystallographic analysis are described in the Supporting Information.

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Supporting Information Available: Crystallographic data for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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