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Equilibrium between (.eta.1-phosphaallyl)- and (.eta.3-phosphaallyl)tungsten complexes

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Fe atoms is smaller and the small shielding effect of the (η^5-C_5H_4)Fe$(CO)_2$ system is more similar to the effect upon the ^{29}Si NMR data of a phenyl group. For example, the chemical shift of Me_3SiPh is at −4.5 ppm relative to Me_4Si, and that of Me_3Si–ferrocenyl is at −3.84 ppm. Given the aromatic nature of the η^5-C_5H_5 group, this similarity in behavior is not entirely unexpected. Overall the ^{29}Si NMR data provide further attractive evidence for significant electron withdrawal from silicon by the Fe atoms in such (η^5-C_5H_5)Fe$(CO)_2$–silyl complexes, which is not evidenced when the silyl groups are bonded to the system via the cyclopentadienyl groups.

In summary, the structural and ^{29}Si NMR data indicate that two transition-metal atoms bonded to a disilane moiety in the 1,2-positions have a capacity to weaken the Si–Si bond. We are currently investigating the chemical and photochemical properties of such complexes in order to demonstrate such activation.

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Registry No. I, 54959-07-8; II, 124944-82-7; Fe, 7439-89-6; Si, 7440-21-3.

Supplementary Material Available: Structure determination summaries and listings of bond lengths and angles, anisotropic displacement coefficients for non-hydrogen atoms, and positional parameters and isotropic displacement coefficients for hydrogen atoms for I and II (10 pages); listings of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Communications

Equilibrium between (η^1-Phosphaallyl)- and (η^3-Phosphaallyl)tungsten Complexes

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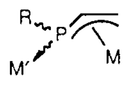
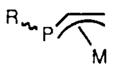
Summary: The reaction of supermesitylvinylhalophosphine (supermesityl = 2,4,6-tri-*tert*-butylphenyl) with (cyclopentadienyl)tricarbonyltungsten hydride in the presence of Et_3N and UV radiation yields [η^1-supermesitylvinylphosphido](cyclopentadienyl)dicarbonyltungsten with a P=W double bond. This η^1-complex isomerizes upon heating to give the corresponding η^3-phosphaallyltungsten complex. The latter is converted back to the η^1-complex upon irradiation with sunlight in CH_2Cl_2.

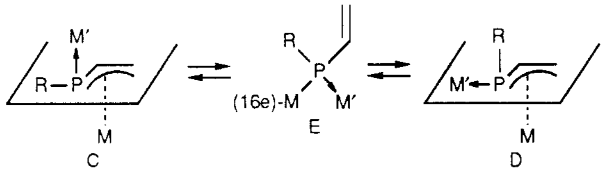
In several recent papers,[1-3] we have described a series of new η^3-phosphaallyl complexes (A). Two questions have arisen during this work: (a) All these complexes are stabilized via an additional η^1-coordination to a metal center. Is it possible to do without this coordination and to prepare "free" η^3-complexes such as B? (b) All these complexes are obtained as mixtures of readily interconverting isomers. A series of X-ray crystal structure analyses have shown that this isomerism originates at phosphorus with either R in the plane of the η^3-phosphaallyl moiety and M,M′ on both sides of this plane (C)[3] or M′ in the plane and M,R on both sides (D).[1] The ready C ⇌ D isomerization (eq 1) suggests an equilibrium between these η^3-complexes and the corresponding 16-electron η^1-complex E with a free C=C double bond. This ready decoordination of the C=C bond could play a crucial role in catalysis. In this work, we describe the first complex of type B and we unambiguously demonstrate the existence of this η^1–η^3 equilibrium (eq 1).





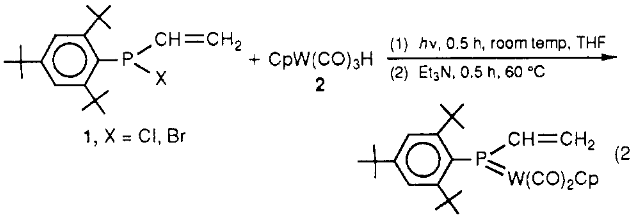
B

A, M = CpFe(CO),[1,2] CpMo$(CO)_2$,[3] CpW$(CO)_2$[3]
M′ = W$(CO)_5$



(1)

Since stable η^3-1,3-diphosphaallyl complexes without additional η^1-coordination at phosphorus had been prepared by Appel[4] using supermesityl (2,4,6-tri-*tert*-butylphenyl) as the P substituent, we chose to study the reaction of the supermesitylvinylhalophosphine 1[5] with the tungsten hydride 2 (eq 2).



1, X = Cl, Br

3 (30%)

(2)

In doing so, we followed a procedure described by Malisch[6] for use in the synthesis of $Cp(CO)_2W{=}PR_2$ complexes, and we were able to obtain such a complex, 3.[7] The presence of the P=W double bond was unambigu-

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[1] Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 357.

[2] Mercier, F.; Hugel-Le Goff, C.; Mathey, F. *Organometallics* 1988, *7*, 955.

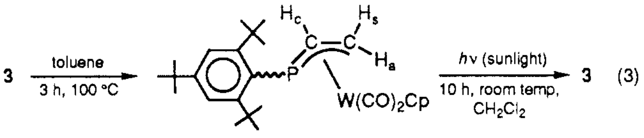
[3] Hugel-Le Goff, C.; Mercier, F.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* 1989, *363*, 325.

[4] See, for example: Appel, R.; Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 420. The work on η^3-1,3-diphosphaallyl complexes has been recently reviewed: Nixon, J. F. *Chem. Rev.* 1988, *88*, 1327.

[5] The synthesis of 1 by reaction of supermesityldichlorophosphine with vinylmagnesium bromide has been described elsewhere: Mercier, F.; Mathey, F. *Tetrahedron Lett.* 1989, *30*, 5269.

[6] Gross, E.; Jörg, K.; Fiederling, K.; Göttlein, A.; Malisch, W.; Boese, R. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 738.

ously established by the very large ^{1}J(P=W) coupling constant of 625 Hz. All the other spectral data of **3** are consistent with those of the already described Cp(CO)$_2$W=PR$_2$ complexes.[6,8] Upon heating, complex **3** is transformed into the η^3-phosphaallyl complex **4**[9] (eq 3).



4 (ca. 50%)

Complex **4** was obtained as a mixture of two isomers (**a**/**b** ca. 80/20). Its formulation as a η^3 complex was unambiguously demonstrated as follows. The mass spectra of **3** and **4** are strictly identical, showing that **4** is an isomer of **3** (both **3** and **4** contain two CO's as demonstrated by IR spectroscopy and elemental analysis). The ^{1}J(P-W) coupling has disappeared in **4**. This feature is very characteristic of the η^{2-5}-phosphaenyl complexes of tungsten.[10] The ^{31}P resonance is shifted to much higher fields (**3**, δ +253; **4a**, δ -48.9 (major); **4b**, δ -28 (minor)). This shift also is very characteristic of π-phospha complexes.[10] Finally, the coordination of the C=C double bond was definitively established by the ^{1}H and ^{13}C NMR spectra. The ^{1}H data thus collected are close to those of a previously described η^1-W(CO)$_5$, η^3-W(CO)$_2$ Cp complex.[3] The ^{1}H-undecoupled ^{31}P NMR spectrum of **4a** shows one broad doublet (J(P-H) = ca. 31 Hz) corresponding to the coupling with H$_s$, whereas the spectrum of **4b** shows a doublet of doublets (J(P-H) = ca. 34 Hz (H$_s$) and 17 Hz). Thus, in the major isomer **4a**, there is no (or only a weak) coupling between H$_c$ and P. Since the η^1,η^3-phosphaallyl isomers C and D are respectively characterized by weak and strong ^{2}J(H$_c$-P) couplings,[1-3] the major isomer of **4** seems to have a structure similar to C with M′ replaced by the phosphorus lone pair.[11]

When **4** is subjected to weak UV irradiation (sunlight, Pyrex flask, CH$_2$Cl$_2$ solution, 10 h at room temperature), it isomerizes back to the starting complex **3** (conversion ratio ca. 80%), thus demonstrating the easy η^1-phosphaallyl $\rightleftharpoons$ η^3-phosphaallyl interconversion.

Registry No. **1** (X = Cl), 124943-01-7; **1** (X = Br), 124943-02-8; **2**, 12128-26-6; **3**, 124943-03-9; **4**, 124943-04-0.

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[7] Complex **3** was purified by chromatography on silica gel with hexane/CH$_2$Cl$_2$ 95/5. **3** is obtained as a blue oil, which slowly crystallizes with 0.5 molecule of hexane; mp 126 °C (dec); ^{31}P NMR (C$_6$D$_6$) δ 253.2 (^{1}J(^{31}P-^{183}W) 625 Hz); ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 1.26 (s, 9 H, Me para), 1.50 (d, ^{5}J(H-P) 0.73 Hz, 18 H, Me ortho), 5.18 (s, 5 H, Cp), 5.57-5.94 (m, 2 H, CH$_2$), 6.78-6.88 (m, 1 H, CH-P), 7.51 (d, ^{4}J(H-P) 2.4 Hz, 2 H, CH meta); IR (Decalin) ν(CO) 1939 (s), 1866 (s) cm^{-1}; mass spectrum (EI, 70 eV, 130 °C, ^{184}W), m/z (rel intensity) 608 (M$^+$, 23), 548 (60), 363 (M$^+$ - Ar, 100), 335 (M$^+$ - Ar - CO, 62), 307 (M$^+$ - Ar - 2CO, 52). Anal. Calcd for C$_{30}$H$_{44}$O$_2$PW: C, 55.31; H, 6.81. Found: C, 54.98; H, 6.23.

[8] See also: Jörg, K.; Malisch, W.; Reich, W.; Meyer, A.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 92. Karsch, H. H.; Reisacher, H.-U.; Huber, B.; Müller, G.; Malisch, W.; Jörg, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 455.

[9] Complex **4** was recrystallized from pentane as an orange solid: ^{31}P NMR (CD$_2$Cl$_2$) δ -48.9 (**4a**), -28.0 (**4b**); ^{1}H NMR (200 MHz, C$_6$D$_6$) **4a** δ 1.20 (s, 9 H, Me para), 1.72 (s, 18 H, Me ortho), 2.73 (ddd, ^{3}J(H-P) 30.2 Hz, ^{2}J(H-H) 2.2 Hz, ^{3}J(H-H) 9.1 Hz, 1 H, H$_s$), 3.89-4.02 (m, 1 H, H$_c$), 4.33 (s, 5 H, Cp), H$_a$ is masked by the methyl resonances; **4b**, δ 1.31 (Me para), 1.72 (Me ortho), 2.78 (dd, ^{3}J(H-P) 35.3 Hz, ^{3}J(H-H) 7.8 Hz, H$_s$), 4.18-4.30 (m, H$_c$), 4.74 (Cp); ^{13}C NMR (CD$_2$Cl$_2$) **4a**, δ 29.88 (d, ^{2}J(C-P) 29.4 Hz, CH$_2$), 69.70 (d, ^{1}J(C-P) 64.5 Hz, CH-P), 91.18 (s, Cp); **4b**, δ 22.40 (d, ^{2}J(C-P) 34.3 Hz, CH$_2$), 89.42 (s, Cp); IR (CH$_2$Cl$_2$) ν(CO) 1935 (vs), 1850 (s) cm^{-1}. Anal. Calcd for C$_{27}$H$_{37}$O$_2$PW: C, 53.34; H, 6.13. Found: C, 53.33; H, 6.07.

[10] Holand, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, *5*, 1413. Deschamps, B.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1985**, 1010.

[11] A free η^3-phosphaallyl cobalt complex with a structure similar to C has been characterized by X-ray analysis. It shows a ^{2}J(H$_c$-P) coupling of only 7 Hz: Mercier, F.; Hugel-Le Goff, C.; Ricard, L.; Mathey, F., to be submitted for publication.

Fluoride-Assisted Reduction of Palladium(II) Phosphine Complexes

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Summary: PdCl$_2$ in the presence of chelating or monodentate arylphosphines reduces in high yields to give Pd(0) phosphine complexes when the reaction is carried out in the presence of n-Bu$_4$NF·3H$_2$O.

Zerovalent palladium phosphine complexes have been extensively studied since their synthesis was first reported by Malatesta in 1957.[1] These compounds are commonly made via the reduction of palladium(II) complexes with use of NaBH$_4$, hydrazine, or KOH/phosphine (for representative examples, see ref 1-5). Although numerous other synthetic routes have been reported, there have been to the best of our knowledge no reports of the reduction of palladium(II) phosphine complexes involving fluoride ion. In this communication we report that palladium(II) in the presence of arylphosphines and fluoride yields zerovalent palladium phosphine complexes via a novel fluoride-assisted redox reaction.

Addition of n-Bu$_4$NF·3H$_2$O (1.41 mmol) to a solution of (Ph$_2$PCH$_2$)$_2$CH$_2$ (1.69 mmol) and PdCl$_2$ (0.564 mmol) in DMSO at 130 °C caused an orange-red solution to form, which rapidly changed to yellow (reaction 1). When the solution was cooled to room temperature, a yellow precipitate formed, which was isolated by filtration. The product, obtained in 91% yield, was identified as Pd[(Ph$_2$PCH$_2$)$_2$CH$_2$]$_2$ by comparison of its ^{31}P and ^{13}C NMR spectra to those of an authentic sample prepared as described previously.[2,3] This assignment was further confirmed crystallographically.[6] Other arylphosphine ligands employed in this reaction gave the known complexes Pd(PPh$_3$)$_4$,[4,7] Pd[(Ph$_2$PCH$_2$)$_2$]$_2$,[5,8] Pd[(Ph$_2$PCH$_2$CH$_2$)$_2$]$_2$,[9] and Pd$_2$[(Ph$_2$P)$_2$CH$_2$]$_3$,[8,10] as well as the new complex Pd[(Ph$_2$PCH$_2$)$_2$CMe$_2$]$_2$.[11] These complexes, ranging in yield from 70 to 90%, were characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. In all cases the NMR data corresponded with published data.

$$\mathrm{PdCl_2} + 3(\mathrm{Ph_2PCH_2})_2\mathrm{CH_2} + 2.5\,n\text{-}\mathrm{Bu_4NF{\cdot}3H_2O} \xrightarrow[130\ ^\circ\mathrm{C}]{\mathrm{DMSO}} \mathrm{Pd[(Ph_2PCH_2)_2CH_2]_2} \qquad (1)$$

The nature of the reducing agent is of interest since reduction does not occur in the absence of fluoride, whether or not water is present. For example, reaction of excess (Ph$_2$PCH$_2$)$_2$ with PdCl$_2$ gave {Pd[(Ph$_2$PCH$_2$)$_2$]$_2$}Cl$_2$[8,12] in 96% yield. Similarly (PPh$_3$)$_2$PdCl$_2$ was isolated in 90% yield when excess PPh$_3$ was reacted with PdCl$_2$.

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[1] Malatesta, L.; Angoletta, M. *J. Chem. Soc.* **1957**, 1186.

[2] Clark, H. C.; Kapoor, P. N.; McMahon, I. J. *J. Organomet. Chem.* **1984**, *265*, 107.

[3] Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1205.

[4] Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

[5] Chatt, J.; Hart, F. A.; Watson, H. R. *J. Chem. Soc.* **1962**, 2537.

[6] Mason, M. R.; Verkade, J. G. Manuscript in progress.

[7] Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

[8] Lindsay, C. H.; Benner, L. S.; Balch, A. L. *Inorg. Chem.* **1980**, *19*, 3503.

[9] Kumobayashi, H.; Mitsuhashi, S.; Akutagawa, S.; Ohtsuka, S. *Chem. Lett.* **1986**, 157.

[10] Stern, E. W.; Maples, P. K. *J. Catal.* **1972**, *27*, 120.

[11] The ligand (Ph$_2$PCH$_2$)$_2$CMe$_2$ was synthesized as described by: Kraihanzel, C. S.; Ressner, J. M.; Gray, G. M. *Inorg. Chem.* **1982**, *21*, 879.

[12] Westland, A. D. *J. Chem. Soc.* **1965**, 3060.

0276-7333/90/2309-0864$02.50/0