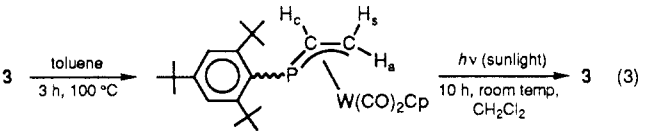
ously established by the very large ^1J(P=W) coupling constant of 625 Hz. All the other spectral data of **3** are consistent with those of the already described Cp-$(CO)_2W{=}PR_2$ complexes.[6,8] Upon heating, complex **3** is transformed into the η^3-phosphaallyl complex **4**[9] (eq 3).



(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 ^1J(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 $^2J(H_c\text{-}P)$ 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_2Cl_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.

(7) Complex **3** was purified by chromatography on silica gel with hexane/CH_2Cl_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_6D_6) δ 253.2 ($^1J(^{31}P\text{-}^{183}W)$ 625 Hz); ^{1}H NMR (200 MHz, C_6D_6) δ 1.26 (s, 9 H, Me para), 1.50 (d, ^5J(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, ^4J(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 $C_{30}H_{44}O_2PW$: C, 55.31; H, 6.81. Found: C, 54.98; H, 6.23.

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(9) Complex **4** was recrystallized from pentane as an orange solid: ^{31}P NMR (CD_2Cl_2) δ -48.9 (**4a**), -28.0 (**4b**); ^{1}H NMR (200 MHz, C_6D_6) **4a** δ 1.20 (s, 9 H, Me para), 1.72 (s, 18 H, Me ortho), 2.73 (ddd, ^3J(H-P) 30.2 Hz, ^2J(H-H) 2.2 Hz, ^3J(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, ^3J(H-P) 35.3 Hz, ^3J(H-H) 7.8 Hz, H_s), 4.18-4.30 (m, H_c), 4.74 (Cp); ^{13}C NMR (CD_2Cl_2) **4a**, δ 29.88 (d, ^2J(C-P) 29.4 Hz, CH_2), 69.70 (d, ^1J(C-P) 64.5 Hz, CH-P), 91.18 (s, Cp); **4b**, δ 22.40 (d, ^2J(C-P) 34.3 Hz, CH_2), 89.42 (s, Cp); IR (CH_2Cl_2) ν(CO) 1935 (vs), 1850 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{37}O_2PW$: C, 53.34; H, 6.13. Found: C, 53.33; H, 6.07.

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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-$Bu_4NF{\cdot}3H_2O$.

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-$Bu_4NF{\cdot}3H_2O$ (1.41 mmol) to a solution of $(Ph_2PCH_2)_2CH_2$ (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

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

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-$[(Ph_2PCH_2)_2CH_2]_2$ 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] $Pd[(Ph_2PCH_2)_2]_2$,[5,8] $Pd[(Ph_2PCH_2CH_2)_2]_2$,[9] and $Pd_2[(Ph_2P)_2CH_2]_3$,[8,10] as well as the new complex Pd-$[(Ph_2PCH_2)_2CMe_2]_2$.[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.

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 $(Ph_2PCH_2)_2$ with $PdCl_2$ gave $\{Pd[(Ph_2PCH_2)_2]_2\}$-Cl_2[8,12] in 96% yield. Similarly $(PPh_3)_2PdCl_2$ was isolated in 90% yield when excess PPh_3 was reacted with $PdCl_2$.

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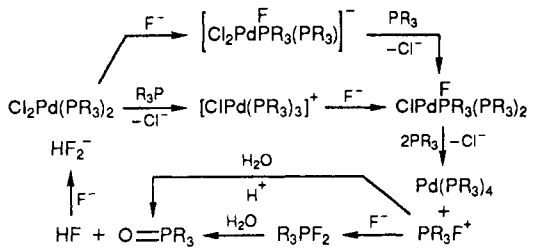
Scheme I



Moreover, reduction failed to take place when water was added to a mixture of PPh_3 and $PdCl_2$ but did occur when fluoride ion was added. The addition of less than a stoichiometric amount of fluoride results in only partial reaction, presumably owing to the formation of the exceedingly stable HF_2^- ion from the protons liberated in the reaction (Scheme I). Analysis of the filtrate of reaction 1 by ^{31}P NMR spectroscopy gave evidence for the formation of the phosphine monoxide $Ph_2P(CH_2)_3P(O)Ph_2$ ($\delta(^{31}P)$ 31.0, -17.2 ppm) as one of two observable oxidation products. The other bidentate phosphines employed also yielded the phosphine monoxides (and not the dioxides) as the final oxidation products. This assignment is unambiguous since $[Ph_2P(O)CH_2]_2$ and $[Ph_2P(O)]_2CH_2$ exhibit singlet ^{31}P NMR resonances, whereas the monoxides $Ph_2PCH_2P(O)Ph_2$ and $Ph_2P(CH_2)_2P(O)Ph_2$ each exhibit two doublets.[13] The filtrates of reaction mixtures of the type exemplified by reaction 1 also contained a difluorophosphorane product. For $(Ph_2PCH_2)_2$, $Ph_2PCH_2CH_2PF_2Ph_2$ was identified by comparison of its ^{31}P and ^{19}F NMR spectroscopic parameters[14] to those previously reported.[15] The difluorophosphorane products for the other ligands employed were similarly identified.[16,17]

A plausible reaction pathway is proposed in Scheme I. Nucleophilic attack of fluoride on phosphorus followed by transfer of two electrons from phosphorus to palladium yields the palladium(0) complex and a fluorophosphonium salt. Although we did not observe fluorophosphonium cations in this reaction, $[Ph_3PF]^+$ has been reported in the literature and it is known to react readily with fluoride in solution to give Ph_3PF_2,[18] which we have identified in our reaction solution. Hydrolysis of the difluorophosphorane to the phosphine oxide completes the scheme. Other pathways, such as prior coordination of fluoride to palladium followed by migration of the fluoride to phosphorus, cannot be ruled out.

We are presently investigating the scope of this reaction using other phosphorus ligands and additional metals, as well as the potential for making it catalytic in fluoride.

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(13) ^{31}P NMR (DMSO): $Ph_2PCH_2P(O)Ph_2$ δ 28.8 (d), -27.1 (d), $^2J_{P-P}$ = 50.5 Hz; $Ph_2PCH_2CH_2P(O)Ph_2$ δ 32.3 (d), -12.4 (d), $^3J_{P-P}$ = 47.3 Hz. For literature values see: (a) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982. (b) Berners-Price, S. J.; Johnson, R. K.; Mirabelli, C. K.; Faucette, L. F.; McCabe, F. L.; Sadler, P. J. *Inorg. Chem.* **1987**, *26*, 3383.

(14) ^{31}P NMR (DMSO): δ -12.4 (d, $^3J_{P-P}$ = 69 Hz), -40.5 (td, $^1J_{P-F}$ = 644 Hz). ^{19}F NMR (DMSO): δ 125.3 (d, $^1J_{P-F}$ = 644 Hz).

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(16) NMR data (compound, $\delta(^{31}P^{III})$, $\delta(^{31}P^{V})$, $^1J_{P-F}$, $^nJ_{P-P}$, $\delta(^{19}F)$, $^3J_{P-F}$): $Ph_2PCH_2PF_2Ph_2$, -23.9 (dt), -41.9 (td), 643 Hz, 63.9 Hz, 136.1 (ddt), 22.5 Hz; $Ph_2P(CH_2)_3PF_2Ph_2$, -17.3 (s), -42.4 (t), 643 Hz, -125.8 (d); $Ph_2P(CH_2)_4PF_2Ph_2$, -15.6 (s), -40.8 (t), 639 Hz; $Ph_2PCH_2CMe_2CH_2PF_2Ph_2$, -23.6 (s), -44.4 (t), 657 Hz; Ph_3PF_2, -54.0 (t), 657 Hz.

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Reductive Acceleration of the Migratory Insertion Reaction: Evidence That Insertion Occurs in a 19-Electron Intermediate

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Summary: The electrochemical reduction of the cobaltacycle $Cp(CO)CoC_{12}H_8$ (**1**) has been studied in tetrahydrofuran/0.1 M Bu_4NPF_6 by cyclic voltammetry, bulk coulometry, and rotating-ring-disk voltammetry. This complex reduces in an irreversible one-electron process at ca. -1.7 V vs SCE. Within the time frame of a CV scan, about $^1/_3$ equiv of the fluorenone anion, Fl^-, is produced per equiv of $\mathbf{1}^-$. Since **1** produces Fl only slowly when heated under CO, it is clear that the reduction of **1** results in an enormous increase in the rate of alkyl to acyl migratory insertion for this complex. Since the insertion must occur immediately after uptake of an electron by **1**, a 19e intermediate is responsible for the enhanced rate of migratory insertion. A body of earlier work on redox acceleration of migratory insertion reactions has led to controversy over whether insertion occurs at the 17e or 19e stage. The present results offer definitive evidence that 19e species may show very large enhancements in their rates of migratory insertions.

Alkyl to acyl migratory insertion reactions are known to be enormously accelerated in odd-electron organometallic complexes.[1-4] However, there is controversy over whether the insertion step occurs in the 17-electron or 19-electron species.[2,5-7] With one exception,[7] redox acceleration of the reaction has been achieved by oxidation of an 18-electron complex in the presence of a nucleophile. Two routes may be envisioned for insertion after formation of the 17e species $[L_nM(CO)(CH_3)]^+$ (Scheme I), depending on whether migration occurs before coordination of Nu (in the 17e radical cation, top route) or after (in the 19e intermediate, bottom route). In spite of very careful experimentation, especially involving Cp(L)Fe(CO)Me (Cp = η^5-C_5H_5),[2,5,6b] no consensus exists on the mechanistic question.

We now report an example of rapid alkyl to acyl migratory insertion in which a 19e complex formed in the absence of an added ligand is the most reasonable structure to precede the insertion step.

The 18e cobaltacycle $Cp(CO)CoC_{12}H_8$[8] (**1**) simplifies the mechanistic possibilities because it is only labile at the Co-CO bond under our conditions.[9] Earlier work showed

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