venience in providing deuterated aldehydes and alcohols through the in situ hydrogen–deuterium exchange of the hydride reagent prior to reduction. The explicit development of anionic transition-metal hydrides as useful synthetic reagents continues to be an attractive goal since, in principle at least, they can be regenerated from inexpensive starting materials: CO and base.

The mechanisms associated with the reduction of acyl chlorides by transition-metal hydrides is still a subject of debate. The reaction of $HFe(CO)_4^-$ and acyl chloride is claimed to involve initial displacement of chloride by $HFe(CO)_4^-$ to form an acyl hydride complex, followed by reductive elimination of aldehyde.[16] The reaction of $CpV(CO)_3H^-$ with acyl chloride has been studied quite extensively, but due to the complex nature of the reaction, the authors failed to reach a definite conclusion as to mechanism.[17] Even the seemingly well-established radical chain process for tributyltin hydride reductions has recently been challenged.[18] We have examined the reaction between $HCr(CO)_5^-$ and $C_6H_5CH_2COCl$ and found neither $C_6H_5CH_3$ nor $C_6H_5CH_2COOCH_2C_6H_5$ among the products (entry 17). Observation of either product can serve as an indication of a radical process.[19] We have also noted a correlation between the rates of acyl chloride reductions and hydridic activity (i.e., the apparent charge polarization in the $M^{\delta+}$–$H^{\delta-}$ bond as implied by ion-pairing studies[20] and hydride-transfer abilities[21]). The relative rate of reaction of $C_6H_5CH_2COCl$ with a range of different transition-metal hydrides was found to be $HW(CO)_4P(OMe)_3^- > HW(CO)_5^- > HCr(CO)_5^- > HFe(CO)_4^-$.[22] This order of reactivity also parallels the hydride-transfer ability of these hydrides toward the reduction of nonhindered alkyl halides.[2] We are inclined to expect that ionic (hydride-transfer) character is associated with the key step in the reductions reported here: however conjecture as to possible intermediates is premature.

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Reaction of (DPPE)Pt(CH_3)(OCH_3) with Tetrafluoroethylene. Synthesis and Structural Characterization of (DPPE)Pt(CH_3)($CF_2CF_2OCH_3$)[†]

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Summary: In order to study the feasibility of catalytic olefin hydration, we prepared (DPPE)Pt(CH_3)(OCH_3) (**1**) by metathesis with $NaOCH_3$ on the (DPPE)Pt(CH_3)Cl precursor. A mixed benzene/methanol solvent system typically resulted in isolated yields of 70%. Complex **1** crystallizes from THF/pentane in space group $P2_1/c$ with cell dimensions a = 11.547 (2) Å, b = 13.152 (6) Å, c = 16.658 (5) Å, and γ = 98.51 (2)° with Z = 4. While complex **1** does not react with unactivated olefins, it does generate small amounts of insertion adducts with acrylonitrile and methyl acrylate. Reaction of **1** with tetrafluoroethylene (TFE) generates a single product in quantitative yield that was identified by spectroscopic methods and by X-ray crystallography as (DPPE)Pt(CH_3)($CF_2CF_2OCH_3$) (**2**); the product expected of olefin insertion into the metal–oxygen bond. TFE adduct **2** also crystallizes in space group $P2_1/c$ with cell dimensions a = 11.764 (1) Å, b = 15.503 (2) Å, c = 16.069 (3) Å, and γ = 105.03 (1)° with Z = 4.

The sometimes severe conditions required for acid-catalyzed olefin hydration and the poor high-temperature thermodynamics of such a reaction make a facile transition-metal-catalyzed route attractive. Low-valent metals capable of activating O–H bonds in water[1] present such a possibility for hydration catalysts if they can coordinate olefins and facilitate olefin insertion into metal–oxygen bonds present.[2] So far, this reaction has been a mere speculation in the Wacker literature.[3] We report here the first example of a late transition-metal alkoxide reacting with an olefin to give the product expected of such an insertion reaction.

In order to study these possible steps, we prepared (DPPE)Pt(CH_3)(OCH_3), 1, by metathesis techniques[4] (eq 1). The complex features a chelating bisphosphine ligand

$$\text{(DPPE)Pt(CH}_3\text{)Cl} + \text{NaOCH}_3 \xrightarrow[25\ ^\circ\text{C, 6 h}]{\text{C}_6\text{H}_6\text{, CH}_3\text{OH}} \underset{\text{1 (75\% yield)}}{\text{(DPPE)Pt(CH}_3\text{)(OCH}_3\text{)}} \quad (1)$$

[†] Contribution No. 3264.

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[3] The insertion of olefins into metal–oxygen bonds as a mechanistic step of the Wacker oxidation is still the subject of some debate. We are unaware of any simple olefin that has been shown to insert into metal–oxygen bonds, though examples of nucleophilic attack of oxy nucleophiles on coordinated olefins are well-known. Relevant articles to this controversy follow: (a) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135–5141. (b) Green, M.; Hancock, R. I. *J. Chem. Soc. A* **1967**, 2054–2057. (c) Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1968**, 464. (d) Stille, J. K.; Fox, D. B. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 157–161. (e) Green, M.; Sashan, J. K. K.; Al-Najjar, I. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1565–71. (f) Clark, H. C.; Goel, A. B.; Goel, S. *J. Organomet. Chem.* **1981**, *216*, C25–C28. (g) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959–60. (h) Stille, J. K.; Devakaruni, R. *J. Am. Chem. Soc.* **1978**, *100*, 1303–4. (i) Zaro, K.; Lautens, M.; Henry, P. M. *Organometallics* **1983**, *2*, 197–9. (j) Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81–7. (k) Gragor, N.; Henry, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 681–2. (l) Henry, P. M. "Catalysis by Metal Complexes"; D. Reidel Publishing Co.: Dordrecht, Netherlands, 1980; Vol. 2.

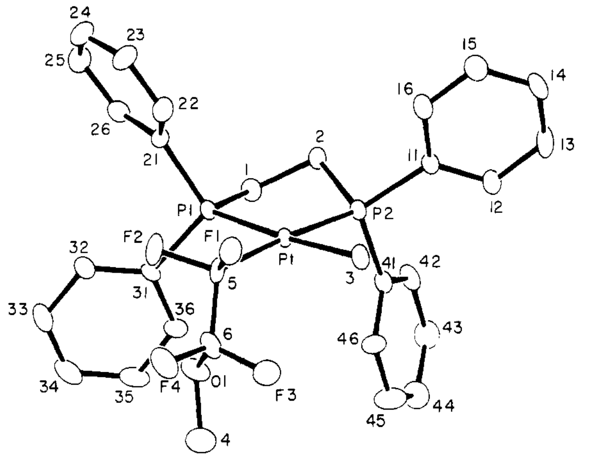

Figure 1. ORTEP drawing of complex 2 shown with 25% probability ellipsoids. Hydrogen atoms omitted for clarity.

to prevent phosphine dissociation from dominating reaction chemistry. Similarly, this complex is a stable Pt(II) model for the potentially catalytic Pt(0)/Pt(II)H(OH) systems. Finally, the methoxide ligand has the advantage of blocking possible complications that might arise from latent OH groups. Metathesis in a mixed benzene/methanol solvent mixture at 25 °C followed by solvent removal and product extraction in THF results in isolated yields of 75% of crude material. Crystallization of 1 from cold THF/pentane solutions yields pure material[5a] suitable for further study.

Complex 1 is a highly moisture- and air-sensitive white solid that reacts with methyl iodide to yield dimethyl ether and (DPPE)$PtCH_3(I)$.[6] The analogous hydroxide complex (DPPE)$PtCH_3(OH)$[4h] can be generated by the combination of 1 and water in THF; a process easily reversed by the addition of methanol to THF solutions of the hydroxide. While 1 reacts with CO to generate (DPPE)$PtCH_3(CO_2CH_3)$,[4e,7] this reactivity does not extend to ethylene or 1-pentene. Reactions of 1 with activated olefins (acrylonitrile and methyl acrylate) produce small amounts (<10%) of materials, tentatively identified by ^1H NMR, as insertion adducts.

Table I. Selected Bond Angles (deg) and Distances (Å) for (DPPE)$PtCH_3(CF_2CF_2OCH_3)$ (2)

Intramolecular Angles

P(1)-Pt-P(2)	84.9 (1)	C(3)-Pt-C(5)	89.7 (3)
P(1)-Pt-C(5)	95.2 (2)	Pt-C(5)-C(6)	114.5 (6)
P(2)-Pt-C(3)	90.4 (2)	C(6)-O(1)-C(4)	115.6 (8)

Interatomic Distances

Pt-P(1)	2.298 (2)	C(6)-O(1)	1.353 (11)
Pt-P(2)	2.258 (2)	O(1)-C(4)	1.457 (13)
Pt-C(3)	2.106 (9)	C(6)-F(ave)	1.377 (11)
Pt-C(5)	2.074 (9)	C(5)-F(ave)	1.399 (10)
C(5)-C(6)	1.541 (14)		

Fortunately, complex 1 reacts cleanly with tetrafluoroethylene (TFE) in THF solution to form an unprecedented new product, 2, in quantitative yield (eq 2). This material

$$\text{(DPPE)Pt(CH}_3\text{)(OCH}_3\text{)} + C_2F_4 \xrightarrow[25\ ^\circ\text{C, 4 h}]{\text{THF, 2 atm}} \text{(DPPE)Pt(CH}_3\text{)(CF}_2\text{CF}_2\text{OCH}_3\text{)} \quad (2)$$

was isolated by solvent removal and identified on the basis of its ^1H and ^{19}F NMR spectra[8] as the species expected of olefin insertion into the metal-oxygen bond of 1. Crystallization of this material by pentane vapor diffusion into THF solutions resulted in acceptable single crystals for X-ray crystallography, which confirmed the anticipated structure (Figure 1).[5b] Representative bond angles and distances are listed in Table I.

This reaction appears general for fluoro olefins,[7] giving, as yet, only partially characterized adducts of hexafluorocyclobutene, octafluorocyclopentene, and hexafluoropropylene in which the olefins have been inserted into the metal-oxygen bond of 1. Interestingly, no olefin or CO insertion into the metal-carbon bond of 1 has been noted. In addition to isolating new fluorinated organometallic ethers, detailed studies into the mechanism of this reaction are in progress.

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Supplementary Material Available: Tables of positional and thermal parameters, estimated standard deviations, estimated atomic parameters, and crystallographers' comments for structures of 1 and 2 (20 pages). Ordering information is given on any current masthead page.

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(5) DPPE = 1,2-bis(diphenylphosphino)ethane. (a) (DPPE)$PtCH_3(OCH_3)$ (fw 639.59): colorless crystals obtained from THF/pentane; monoclinic, $P2_1/c$, $a = 11.547$ (2) Å, $b = 13.152$ (6) Å, $c = 16.658$ (5) Å, $\beta = 98.51$ (2)°; $V = 2502$ Å^3; temp = −100 °C; d(calcd) = 1.698 g cm^{-3} for $Z = 4$; 4071 diffractometer reflections (Mo Kα) [$I \geq 2\sigma(I)$] corrected for adsorption ($\mu = 58.095$ cm^{-1}, Gaussian grid 8 × 8 × 8); full-matrix anisotropic refinement on 289 variables yielded $R = 0.666$ and $R_w = 0.073$. (b) (DPPE)$PtCH_3(CF_2CF_2OCH_3)$ (fw 739.61): colorless crystals obtained from THF/pentane; monoclinic $P2_1/c$, $a = 11.764$ (1) Å, $b = 15.503$ (2) Å, $c = 16.069$ (3) Å, $\beta = 105.03$ (1)°; $Z = 4$; 4290 diffractometer reflections [$I \geq 2\sigma(I)$] (Mo Kα) corrected for absorption ($\mu = 51.67$ cm^{-1}); full-matrix anisotropic refinement on 343 variables converged with $R = 0.045$ and $R_w = 0.048$.

(6) As identified by ^1H and ^{31}P NMR as found in ref 4h. The reaction of CD_3I with 1 generates CD_3OCH_3 as identified by ^1H and ^2H NMR and by GC/MS.

(7) The mechanism of these apparent insertion reactions is under investigation.

(8) ^1H data (THF-d_8/THF-d_7): δ 0.690 (3 H, t with Pt satellites, $J_{HP} = 7.05$ Hz, $J_{HPt} = 69.68$ Hz), 2.25 (4 H, m, br), 3.22 (3 H, s), 7.4–7.8 (20 H, 3 m of aromatic protons). ^{19}F data (THF-d_8/F-11 external): δ −87.61 (2 F, tt with Pt satellites, J_{FF} = very small br, $J_{FP_{1,2}} = 31.71$ Hz, $J_{FPt} = 400.96$ Hz), −90.860 (2 F, q with Pt satellites, J_{FH} = very small br, $J_{FPt} = 41.5$ Hz). ^{31}P data (THF-d_8, H_3PO_4 external): δ 48.578 (1 P, t with Pt satellites, $J_{PF} = 32.0$ Hz, $J_{PPt} = 1798$ Hz), 45.985 (1 P, dd with Pt satellites, $J_{PF_1} = 2.80$ Hz, $J_{PF_2} = 37.2$ Hz, $J_{PPt} = 1966$ Hz).