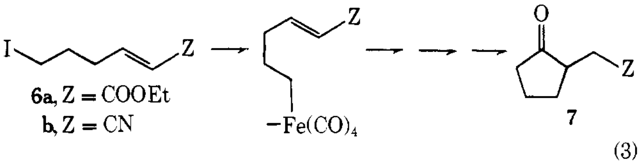
intramolecular insertions. Treatment of **6** with $Na_2Fe(CO)_4$ in THF gave after protonation cyclopentanone derivatives **7a** and **7b** in 85 and 82% yield, respectively (eq 3). We are currently investigating other applications of this novel approach to ring construction.



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(6) A typical example is shown in the preparation of ethyl 4-ketooctanoate from ethyl acrylate and butyl iodide. A slurry of $Na_2Fe(CO)_4$ in 20 mL of dry THF was prepared by reduction of 185 μL (1.4 mmol) of $Fe(CO)_5$ with 2 mL of 1% sodium amalgam.[3] The vessel was purged with N_2 to remove CO, cooled via an ice bath, and treated with 250 μL (2.5 mmol) of ethyl acrylate and then with 120 μL (1 mmol) of 1-iodobutane. The N_2 atmosphere was maintained throughout. The mixture was stirred at room temperature for 4 h, whereupon it was treated with 0.12 mL of HOAc, stirred for 5 min, poured into water and twice extracted with ether. The concentrated extracts were filtered through a short plug of Al_2O_3 (neutral) to remove iron residues. Bulb-to-bulb distillation gave 156 mg (80%) of $C_4H_9COCH_2CH_2COOEt$.

(7) Acylferrates are most conveniently prepared by the addition of CO or Ph_3P to **1**,[3] the addition of acid chlorides to $Na_2Fe(CO)_4$,[4] or by the addition of alkyllithium reagents to $Fe(CO)_5$: W. O. Siegl and J. P. Collman, *J. Am. Chem. Soc.*, **94**, 2516 (1972).

(8) A structure involving σ bonding through oxygen is also plausible but a π-enolate complex seems unlikely insomuch as the required evolution of CO for π participation is not observed.

(9) A similar band is observed at 1585 cm^{-1} when ethyl acrylate is employed.

(10) Similar results were obtained with commercial $Na_2Fe(CO)_4$ (Ventron Corp.).

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Ditertiary Phosphines as Monodentate Ligands in Transition Metal Carbonyl Complexes

Sir:

Early syntheses of group 6 transition metal carbonyl complexes containing tetraphenyldiphosphinoethane typically involved thermal or photolytic methods, and under these harsh conditions only chelated complexes were isolated. The synthesis of a tungsten carbonyl complex which contains $Ph_2PCH_2CH_2PPh_2$ as a monodentate ligand was reported in 1972 and was achieved by displacing aniline of $(OC)_5WNH_2Ph$ with the phosphine at room temperature.[1]

$$(OC)_5WNH_2Ph + PPh_2CH_2CH_2PPh_2 \rightarrow (OC)_5WPPh_2CH_2CH_2PPh_2 + PhNH_2$$

This reaction has been employed subsequently in the synthesis of a number of carbonyl complexes which contain both symmetrical and unsymmetrical ditertiary phosphines.[2]

The reaction of a pentacarbonylhalo metal anion with a ditertiary phosphine in the presence of trialkyloxonium tetrafluoroborate has been reported as an alternate method for the preparation of complexes of this type.[3]

$$(OC)_5MX^- + PPh_2CH_2CH_2PPh_2 + (R_3O)(BF_4) \rightarrow (OC)_5MPPh_2CH_2CH_2PPh_2 + RX + R_2O + BF_4^-$$

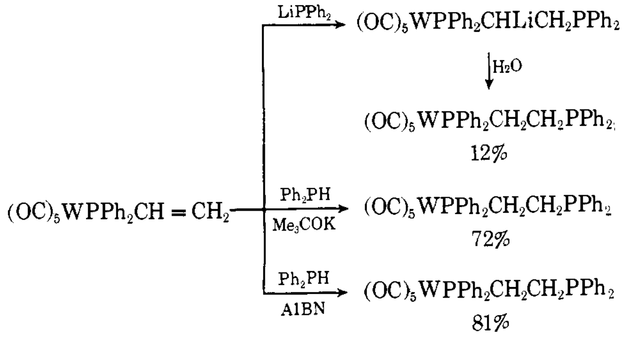
Careful evaluation of the foregoing approaches shows that neither is satisfactory. In each reaction substantial quantities of dimetallic decacarbonyl, $(OC)_5WPPh_2CH_2CH_2PPh_2W(CO)_5$, and unreacted free ligand must be separated from the desired product. The formation of the dimetallic product is inevitable since $(OC)_5WPPh_2CH_2CH_2PPh_2$ is itself a good ligand and competes well for available metal sites.[4] An additional disadvantage of both methods is that there is no means of controlling which end of an unsymmetrical ditertiary phosphine will coordinate to the metal. Further, since alkyloxonium salts are good alkylating agents, any excess of this reagent quaternizes the free phosphine.

It was desirable, therefore, to find a method for coordinating one end of a polytertiary phosphine to a metal in high yield or for converting a monodentate ligand of a transition metal complex into a polydentate ligand thereby accomplishing the same thing. We have explored the latter approach by investigating the reaction of diphenylphosphine with pentacarbonyldiphenylvinylphosphinetungsten(0).

The addition of secondary phosphines to vinylphosphines has been studied previously by several groups. Grim and coworkers have used the addition of lithium alkyl and aryl phosphides to vinylphosphines for the preparation of unsymmetrical ditertiary phosphines.[2] King et al. have shown that the addition of secondary phosphines to vinylphosphines is base catalyzed and have prepared a number of polyphosphines by this method.[5] More recently Meek and coworkers have determined that these addition reactions are free radical catalyzed and applicable to a wide range of systems.[6]

We have determined that these approaches to the synthesis of polytertiary phosphines also are effective when a transition metal carbonyl complex which contains a vinylphosphine is employed as a reactant (Scheme I). The reaction of a THF solution of lithium diphenylphosphide with $(OC)_5WPPh_2CH{=}CH_2$ (mp 64–65 °C) followed by hydrolysis is the least reliable of the three reactions and gives an average yield of 12% (based on eight reactions). Stoichiometric quantities of diphenylphosphine react with

Scheme I



$(OC)_5WPPh_2CH{=}CH_2$ in THF in the presence of catalytic quantities of potassium *tert*-butoxide for 2 h at refluxing temperatures to give an average yield of 72% (based on five reactions). When stoichiometric quantities of $(OC)_5WPPh_2CH{=}CH_2$ and diphenylphosphine are heated without solvent in the presence of catalytic amounts of AIBN (2,2′-azobisisobutyronitrile) at 75 °C for 24 h followed by vacuum removal of volatile components at 80 °C for 2 h, an average yield of 81% is realized (based on five reactions). The product, $(OC)_5WPPh_2CH_2CH_2PPh_2$, was purified by recrystallization from dichloromethane and methanol and characterized by comparing the melting point, infrared spectrum, and ^{31}P NMR spectrum with those of known material.[1]

We judge the base-catalyzed and free-radical-catalyzed reactions to be equally valuable, whereas the lithium diphenylphosphide addition is not recommended. The free-radical-catalyzed reaction has the additional advantage of not requiring a solvent.

Methods of controlling the number of metal sites to which a polydentate ligand becomes attached upon reaction with a metal complex are not well developed. Our preliminary results indicate that the desired coordination may be best achieved by building the polyphosphine from a vinylphosphine ligand on the transition metal complex of interest. This approach should be limited only by the lability of the complex and the susceptibility to attack of other attached ligands under the experimental conditions employed. We are currently exploring the generality of this method with a number of vinylphosphines and metal carbonyls.

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Synthesis and Characterization of $HOs_3(CO)_{10}(CH_3)$, $H_2Os_3(CO)_{10}(CH_2)$, and $H_3Os_3(CO)_9(CH)$. Interconversion of Cluster-Bound Methyl and Methylene Ligands[1]

Sir:

Indirect evidence suggests that a tautomeric interconversion between methyl and hydrido methylene ligands can be a significant reaction pathway for methyl-transition metal compounds.[2]

$$M(CH_3) \rightleftarrows HM(CH_2)$$

This equilibrium also is featured in mechanistic interpretations of reactions involving methane and metal surfaces, e.g., H/D exchange, hydrocarbon hydrogenolysis, and methanation of carbon monoxide.[3] We wish to report the first direct observation of interconverting methyl and methylene ligands in the form of the cluster compounds $HOs_3(CO)_{10}(CH_3)$ (**1**) and $H_2Os_3(CO)_{10}(CH_2)$ (**2**) and also their transformation into the compound $H_3Os_3(CO)_9(CH)$ (**3**).

Previous work[4] with $HOs_3(CO)_{10}CH_2C(O)OEt$, prepared from $H_2Os_3(CO)_{10}$ and ethyl diazoacetate, suggested examination of diazo compounds not possessing a potential coordinating group. Treatment of a purple dichloromethane solution of $H_2Os_3(CO)_{10}$ with 1 equiv of ethereal diazomethane at room temperature quickly (10 min) resulted in a yellow solution. Workup by preparative TLC (hexane/silica gel) provided a single product, isolated as a yellow, air-stable solid (77%). The low resolution, electron-impact mass spectrum of the material suggested the formulation "$Os_3(CO)_{10}(CH_4)$", which was confirmed by high resolution measurement of the molecular ion (obsd 871.872, calcd 871.865, for ^{192}Os = 191.962 amu).

NMR data collected for "$Os_3(CO)_{10}(CH_4)$" in solution revealed a mixture of the isomers $HOs_3(CO)_{10}(CH_3)$ (**1**) and $H_2Os_3(CO)_{10}(CH_2)$ (**2**). Thus, in the ^1H NMR spectrum ($CDCl_3$), **1** shows a narrow doublet at τ 13.68 and a weak quartet at 25.02 (ratio 3:1, J = 0.35 Hz), whereas **2** displays two multiplets at low field (τ 4.88 (H_a), 5.68 (H_b)) and two at high field (25.38 (H_c), 30.71 (H_d)), each hydrogen in the molecule being coupled to the other three (J_{ab} = 5.9, J_{ac} = 3.0, J_{ad} = 2.1, J_{bc} = 0.7, J_{bd} = 2.4, J_{cd} = 0.8 Hz). In the ^{13}C NMR spectrum of "$Os_3(CO)_{10}(^{13}CH_4)$", prepared from ^{13}C-enriched diazomethane, the methyl quartet (J_{CH} = 121 Hz) for **1** appears upfield of TMS (−14.9 ppm), and displays a small additional coupling ($J_{CH'}$ = 2.5 Hz) due to the hydride ligand. The methylene carbon in **2** is observed as a double doublet (J_{CH_a} = 143, J_{CH_b} = 140 Hz) at 25.8 ppm, also with one small additional coupling (J_{CH_c} = 3 Hz). The equilibrium constant $K = [\mathbf{2}]/[\mathbf{1}] = 3.5 \pm 0.1$ (CD_2Cl_2, 32 °C), when calculated from either ^{13}C or ^1H NMR signal intensities. The value of K shows a pronounced dependence on solvent, decreasing in the order acetone > dichloromethane > benzene, but it changes little with temperature (e.g., toluene , 30–115 °C).

It has proved possible to demonstrate the interconversion of **1** and **2** in several ways. Thus, spin saturation transfer[5] experiments conducted at several temperatures below ~115 °C showed that irradiating appropriate signals of either isomer produced significant loss of intensity (up to 25%) in signals due to the nonirradiated isomer. Furthermore, when the addition of diazomethane to $H_2Os_3(CO)_{10}$ was conducted at −20 °C and monitored by ^1H NMR, only the signals associated with the hydrido methyl compound **1** appeared. Upon raising the temperature these signals decreased in intensity as the signals due to **2** grew in ($k(\mathbf{1} \rightarrow \mathbf{2}) \sim 1 \times 10^{-3}\ s^{-1}$, $\Delta G^{\ddagger} \sim 20$ kcal/mol, at 14 °C). Finally, when $PPhMe_2$ (<1 equiv) was added to a mixture of **1** and **2** at −10 °C, where equilibration is slow, only **1** appeared to react. Raising the sample temperature to 25 °C reestablished the equilibrium ratio as part of **2** converted into **1**. Only $Os_3(CO)_{10}(PPhMe_2)_2$ and methane were observed as products; no evidence for the expected adduct $HOs_3(CO)_{10}(PPhMe_2)(CH_3)$[6] was obtained.

Heating a nitrogen-flushed solution of **1** and **2** in toluene or xylene at 110 ° for 24 h generated a new compound that was isolated in good yield as an air-stable, nearly colorless solid following preparative TLC (silica gel/pentane). Formulation of this material as the methylidyne compound $H_3Os_3(CO)_9(CH)$ (**3**) is supported by ^1H NMR (CH_2Cl_2, τ 0.64 (q, 1 H), 30.02 (d, 3 H, J = 1.1 Hz)) and low resolution mass (m/e 844, M^+ (^{192}Os) and $(M - xCO)^+$, x = 1–9)) spectroscopic data. The ^{13}C NMR signal of $H_3Os_3(CO)_9(^{13}CH)$ occurs at