$(OC)_5WPPh_2CH{=}CH_2$ 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).

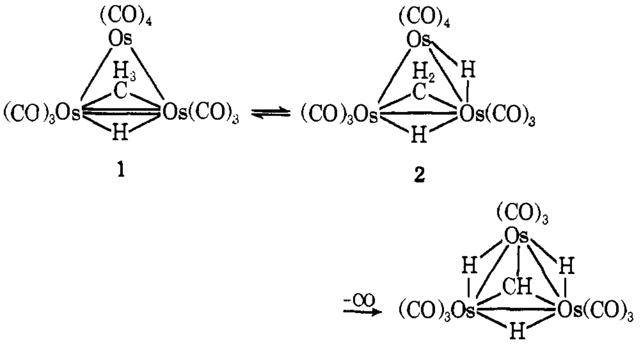
NMR data collected for "$Os_3(CO)_{10}(CH_4)$" in solution revealed a mixture of the isomers $HOs_3(CO)_{10}(CH_3)$ (**1**) and $H_2Os_3(CO)_{10}(CH_2)$ (**2**). Thus, in the ^1H NMR spectrum ($CDCl_3$), **1** shows a narrow doublet at τ 13.68 and a weak quartet at 25.02 (ratio 3:1, $J = 0.35$ Hz), whereas **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

68.2 ppm ($(CD_3)_2CO$) with $J_{CH} = 171$ and $J_{CH'} = 3$ Hz.

Reasonable structures may be proposed for **1**, **2**, and **3**, as shown below. Compound **3** appears entirely analogous to the previously known ethylidyne compound $H_3Os_3(CO)_9(CCH_3)$.[7]



1 **2** **3**

The structure for **2** incorporates features displayed by $HOs_3(CO)_{10}(CHCH_2PPhMe_2)$[8] and $H_2Os_3(CO)_9(C{=}CH_2)$.[9,10] Although the ^1H and ^{13}C NMR signals observed for the bridging methylene in $[CpMn(CO)_2]_2CH_2$ (τ 1.35, 153 ppm)[11a] are downfield of those for **2**, the analogous signals for the terminal methylene in $Cp_2Ta(CH_3)(CH_2)$ (−0.22, 228 ppm)[11b] are even further downfield. The structure proposed for **1** is least certain but modeled after that established for $H_2Os_3(CO)_{10}$.[12] Alkyl ligands bridging two transition metals are rare, but not unknown,[13] and the upfield position of the ^1H NMR signal for the methyl ligand in **1** is quite distinct from the positions for the methyl groups in the series,[14] $HOs(CO)_4(CH_3)$, $HOs_2(CO)_8(CH_3)$, and $Os_3(CO)_{12}(CH_3)_2$ (all about τ 9.7).[15] Studies in progress are aimed at further characterizing the structures of **1** and **2** as well as the reactivity of all three compounds.[20]

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The possibility that the methyl ligand in **1** is terminal but experiences an anisotropic field generated by the osmium–osmium double bond cannot be eliminated. However, we note that the terminal methyl ligands in $[WMe(NEt_2)_2]_2$, which are adjacent to a tungsten–tungsten triple bond, do not show ^1H (or ^{13}C) NMR signals shifted to unusually high field.[17]

Another possible explanation for the high-field signal would be a structure involving an unsymmetrical Os—C···H···Os bridge. There is a broad band at 2520 cm^{-1} in the infrared spectrum of "$Os_3(CO)_{10}(CH_4)$", both in a KBr pellet and in CCl_4 solution. However, the band does not diminish in intensity nor appear at a lower frequency in the spectrum of "$Os_3(CO)_{10}(CH_2D_2)$", which may indicate that it is a combination of $\nu_{CO} + \nu_{MC}$. The methyl ^1H NMR signal of **1** is somewhat broader at −80 °C than at −20 °C (relative to the internal TMS signal), but solubility problems have prevented us from operating at lower temperatures. Thus, at present there is no evidence, of the sort obtained for the molybdenum pyrazolylborate complexes,[18,18] that a C—H···Os interaction exists.

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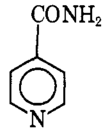
Electron Transfer. 28. A Four-Membered in Vitro Electron-Transport Chain

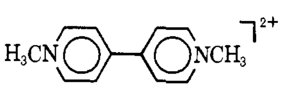
Sir:

Although the formal similarity between in vivo electron-transport chains and electron-transfer reactions catalyzed by an external organic species in solution has been noted,[1] the latter processes may at best be considered highly abbreviated models of the bio systems, for they involve, aside from the metal ion centers furnishing the driving force for net reaction, only a single catalytic intermediary. We here report expansion of the in vitro electron-transfer chain to four members by inclusion of two catalysts, exhibiting a combined action far more marked than the sum of their individual effects.

Table I lists the rates at which $Co(en)_3^{3+}$ is reduced by Eu^{2+} in the absence of catalysis and in the presence of isonicotinamide (IN) alone and methyl viologen (MV) alone, and in the presence of both.



IN



MV

Table I. Catalyzed Reductions of $Co(en)_3^{3+}$ by Eu^{2+}, 25 °C

[Isonicotinamide], M	[Methyl viologen], M	Rate, M $s^{-1} \times 10^6$ [a]
0	0	0.01
0.0127	0	2.3
0	5.13×10^{-4}	7.8
0.0127	5.13×10^{-4}	84

[a] Reactions were carried out in 1 M $HClO_4$: [Eu^{2+}], 0.020 M; [Co^{III}], 0.00167 M; [Eu^{3+}], 0.03 M. Reaction progress was monitored spectrophotometrically at 465 nm.[1]