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Formation of μ -Silylene μ -Hydrido Manganese–Platinum Heterobimetallics via Oxidative Addition of $(OC)_5MnSiR_2H$ to Zerovalent Platinum Compounds and the Structure of $(OC)_4Mn(\mu-PPh_2)(\mu-H)PtPh(PPh_3)$, a Product of a Solvolysis of a Silylene Bridge

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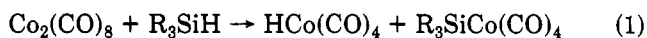
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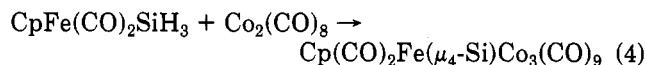
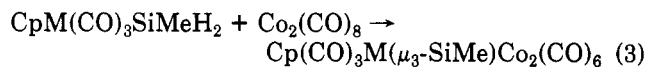
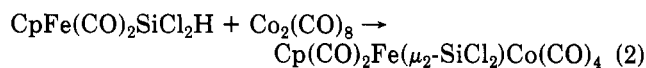
The complexes $(OC)_5MnSiR_2H$ ($R = Me, Ph, Cl$) react with $Pt(C_2H_4)(PPh_3)_2$ or $Pt(PPh_3)_4$ via oxidative addition of the Si–H bond across Pt to give the μ -silylene μ -hydrido complexes $(OC)_4Mn(\mu-SiR_2)(\mu-H)Pt(PPh_3)_2$. These complexes react with PEt_3 to give $(OC)_4Mn(\mu-SiR_2)(\mu-H)Pt(PEt_3)_2$, react reversibly with CO to give $(OC)_4Mn(\mu-SiR_2)(\mu-H)Pt(PPh_3)(CO)$, and react with MeOH or H_2O to give $(OC)_4Mn(\mu-PPh_2)(\mu-H)PtPh(PPh_3)$ (**8**) (a product of P–Ph bond cleavage). The structure of **8** has been determined by single-crystal X-ray diffraction. Complex **8** is monoclinic, space group $P2_1/c$, with $a = 12.929$ (2) Å, $b = 26.382$ (5) Å, $c = 11.245$ (2) Å, $\beta = 110.52$ (1)°, $V = 3592$ Å³, and $D_{calcd} = 1.63$ g cm⁻³ for $Z = 4$. The structure was refined to $R = 0.0348$ and $wR = 0.0460$ for the 4763 reflections with $I > 3\sigma(I)$. The structure of **8** consists of distorted pseudo-square-planar Pt and pseudooctahedral Mn centers with trans phenyl and hydride ligands on Pt. The Mn and Pt atoms are separated by 2.864 (1) Å and bridged by μ -PPh₂ and μ -H ligands. The position of the μ -H was located and refined. Associated bond lengths are Pt–H = 1.64 (8) Å and Mn–H = 1.80 (8) Å; $\angle PtHMn = 113$ (4)°.

Introduction

A wide variety of compounds containing transition-metal–silicon bonds are known.^{1,2} One general synthetic method involves oxidative addition of organosilanes, R_3SiH , to low-valent transition-metal complexes.^{1–3} The first example of such a reaction was reported by Chalk and Harrod³ (eq 1). This method was later widely used to



synthesize many transition-metal–silyl compounds.^{1,2} However, while the oxidative addition of R_3SiH to transition metals has been shown to be feasible under mild thermal and photochemical conditions, there are only a few examples reported where an organometallic silane, $[M]-SiR_2H$, has been utilized. Thus eq 1 may be modified to give a series of μ -silylene heterometallic compounds (e.g. eq 2–4).⁴



Significantly absent from this approach to μ -silylene systems are simple two-electron oxidative addition processes. In this paper we report the synthesis and reactions of the heterobimetallic complexes $(CO)_4Mn(\mu_2-SiR_2)(\mu_2-H)Pt(PPh_3)_2$ (**1**), which were obtained from the two-electron oxidative addition of the Si–H bond of $Mn(CO)_5SiR_2H^5$ across $Pt(C_2H_4)(PPh_3)_2$.⁶ Simple organo-

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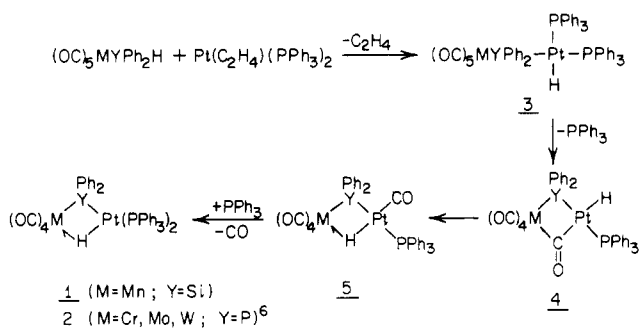
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Table I. Spectroscopic and Analytical Data for MnPt Heterobimetallic Complexes

| complex | infrared $\nu(\text{CO})^a$, cm^{-1} | ^1H NMR hydrido ligand (CD_2Cl_2 soln) | | | $^{31}\text{P}\{^1\text{H}\}$ NMR (ppm rel to H_3PO_4) ^c | | | | | elemental anal. found (calcd) | | isolated yield, % | |
|---------|---|--|--|--|---|----------------------|----------------------|----------------------------|--------------------|----------------------------------|---------------|-------------------------|----|
| | | $\delta, ^b$ ppm | $J_{^{31}\text{P}(\text{cis})-\text{H}}$ | $J_{^{31}\text{P}(\text{trans})-\text{H}}$ | $J_{^{195}\text{Pt}-\text{H}}$ | $\delta(\text{P}^1)$ | $\delta(\text{P}^2)$ | $J_{\text{P}^1\text{P}^2}$ | J_{PtP^1} | J_{PtP^2} | C | | H |
| 1a | 2063, 1985, 1970, 1959 | -8.56 | 33 | 77 | 494 | 20 | 33 | 15.2 | 1740 | 4386 | 53.33 (53.51) | 3.94 (4.01) | 62 |
| 1b | 2035, 1958, 1944, 1929 | -9.10 | 31 | 78 | 490 | 19 | 32 | 18.5 | 1716 | 4264 | 58.33 (57.50) | 3.86 (3.84) | 66 |
| 1c | 2051, 1977, 1962, 1952 | -9.57 | 29 | 70 | 460 | 15 | 30 | 14.5 | 1813 | 4378 | 48.69 (48.48) | 3.16 (3.37) | 60 |
| 6 | 2064, (1994), ^d 1971, 1963, 1952 | -8.7 (br) ^e | | (br) ^e | 510 | 8 | ... | ... | ... | 3300 | | | 52 |
| 7 | 2033, 1956, 1935, 1923 | -10.3 | 30 | 71 | 424 | not recorded | | | | | 43.5 (43.04) | 4.95 (5.25) | 68 |
| 8 | 2068, 1991, 1984, 1956 | -12.6 | { ^f 14/ 19} | ... | 370 | {124/ 21} | | 311 | {2282/ 2771} | | 55.04 (54.41) | 3.64 (3.52) | 50 |

^aSolvent cyclohexane. ^bAll resonances are doublets of doublets unless otherwise stated. ^cP¹ trans and P² cis to the SiR₂ unit. ^dDue to $\nu(\text{PtCO})$. ^eExchange between coordinated and a small amount of free PPh₃ impurity. ^f μ -PPh₂.

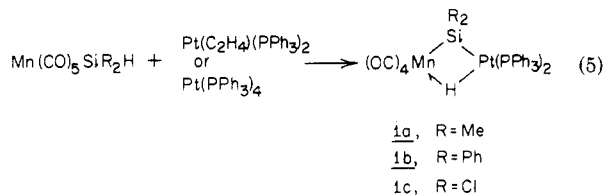
Scheme I



silanes are known to be reactive with Pt(0) compounds.⁷ This study was performed to investigate further the role of metal-assisted CO labilization and intramolecular hydride transfer in heterobimetallic-hydrido carbonyl chemistry, and represents a development of previous work with μ -phosphido analogues.⁶

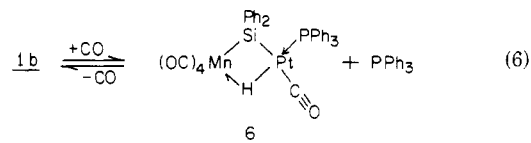
Results and Discussion

The reaction of $\text{Mn}(\text{CO})_5\text{SiR}_2\text{H}$ ($\text{R} = \text{Me, Ph, Cl}$)⁵ with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ or $\text{Pt}(\text{PPh}_3)_4$ at room temperature gives the μ -silylene μ -hydrido complexes 1 as the final product (eq 5). Complexes 1 were isolated in good yields as yellow, crystalline, air-stable (up to a few days in the solid state), but moisture-sensitive materials and were fully characterized by ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR, IR spectroscopy, and elemental analysis (Table I). Thus for example, the ^1H NMR of 1a exhibits an upfield 12-line pattern at $\delta = -8.56$ ppm assignable to hydride ligand. The magnitude of $J_{^{31}\text{P}(\text{trans to H})-\text{H}}$ (77 Hz) is typical for a phosphine trans to a bridging hydride and $J_{^{195}\text{Pt}-\text{H}}$ (494 Hz) is also within the range expected for a bridging hydride.⁶ The isolation of 1 (eq 5) parallels the formation of the isostructural μ -



phosphido μ -hydrido analogue $(\text{OC})_4\text{Cr}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Pt}(\text{PPh}_3)_2$ (2; $\text{M} = \text{Cr}$) which is obtained via an oxidative addition of the P-H bond of $\text{Cr}(\text{CO})_5(\text{PPh}_2)\text{H}$ to $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ followed by platinum-assisted CO loss

(Scheme I).⁶ When the NMR data for $(\text{OC})_4\text{Cr}(\mu\text{-PPh}_2)(\mu\text{-H})\text{Pt}(\text{PPh}_3)_2$ (2) are compared with those of $(\text{OC})_4\text{Mn}(\mu\text{-SiPh}_2)(\mu\text{-H})\text{Pt}(\text{PPh}_3)_2$ (1b), the following significant changes in coupling constant data (Hz) are observed [$2 \{ \text{M} = \text{Cr} \}$ (1b)]: $J_{^{195}\text{Pt}-\text{H}} = 648$ (490); $J_{^{31}\text{P}(\text{trans to H})-\text{H}} = 107$ (78); $J_{^{195}\text{Pt}-^{31}\text{P}(\text{cis to H})} = 2312$ (1716); $J_{^{195}\text{Pt}-^{31}\text{P}(\text{trans to H})} = 3494$ (4264). The ca. 25% decrease in $J_{^{195}\text{Pt}-\text{H}}$ and $J_{^{31}\text{P}(\text{trans to H})-\text{H}}$ suggest a weaker Pt-H(μ) interaction in 1b vis-à-vis 2 ($\text{M} = \text{Cr}$) while the 22% increase in $J_{^{195}\text{Pt}-^{31}\text{P}(\text{trans to H})}$ is indicative of a stronger Pt-PPh₃ (trans to H) bond in 1b. The low value of $J_{^{195}\text{Pt}-^{31}\text{P}}$ for the PPh₃ ligand trans to the μ -SiPh₂ (cis to H; 1b) is consistent with the known high trans influence of silyl ligands.⁸ Reaction of the μ -silylene μ -hydrido complex 1b with CO in hexanes leads to the reversible formation of 6, as detected by IR studies of the $\nu(\text{CO})$ region (see eq 6). Particularly di-



agnostic is the observation of a $\nu(\text{CO})$ absorption at 1994 cm^{-1} assignable to Pt(CO). Removal of CO regenerates 1. By working under a CO atmosphere, it proved possible to isolate complex 6 (contaminated with a small amount of PPh₃) (see Table I for IR and NMR data). Owing to exchange between free and coordinated PPh₃, $J_{^{31}\text{P}-\text{H}}$ coupling to the hydrido ligand of 6 was not resolved. However, the $J_{^{195}\text{Pt}-\text{H}}$ of 510 Hz is consistent with a μ -hydrido structure while the $J_{^{195}\text{Pt}-^{31}\text{P}}$ of 3300 Hz is more consistent with PPh₃ trans to μ -H (a value <2000 Hz would be expected if the PPh₃ were trans to μ -SiPh₂) and suggests that CO substitutes the PPh₃ ligand trans to μ -SiPh₂ (eq 6) which is consistent with the high trans influence of silyl ligands.⁸ In contrast to the formation of $(\text{OC})_4\text{M}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Pt}(\text{PPh}_3)_2$ (2) for which the intermediates 3-5 could be identified (Scheme I, $\text{Y} = \text{P}$)⁶ no corresponding intermediates were identified during NMR and IR monitoring of the reaction of $\text{Mn}(\text{CO})_5(\text{SiR}_2\text{H})$ with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ to give 1 (eq 5). However, given the structural and chemical similarity of $\text{Mn}(\text{CO})_5(\text{SiR}_2\text{H})$ and $\text{M}(\text{CO})_5(\text{PPh}_2)\text{H}$ it is highly likely that both 1 and 2 are formed by similar reactions pathways (Scheme I). Indeed the postulated intermediates 3, 4, and 5 (Scheme I, $\text{Y} = \text{Si}$) should be short-lived (and hence not observed) since the combined high trans influence of the silyl and terminal hydride ligand in 3 should facilitate the ligand substitutions shown. The oxidative addition of the Si-H bond of $\text{Mn}(\text{CO})_5(\text{SiR}_2\text{H})$ to $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ is the probable rate-determining step in the formation of 1. Complex 1b reacts with 2PEt_3 to

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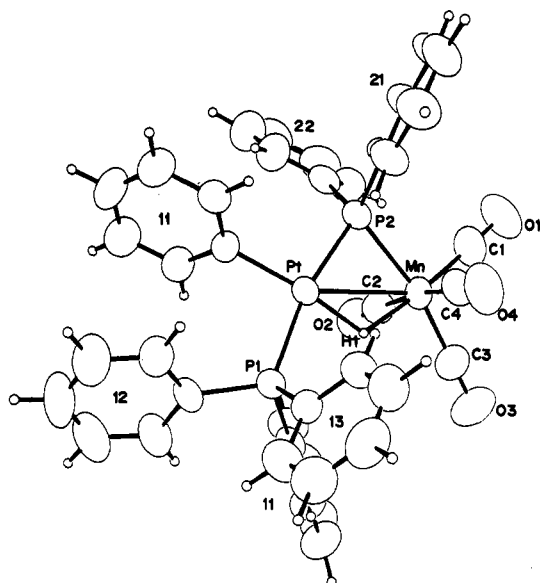
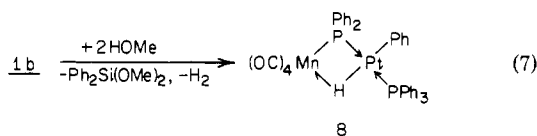


Figure 1. Molecular structure of $(OC)_4Mn(\mu-PPh_2)(\mu-H)PtPh(PPh_3)$ (**8**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are drawn with uniform isotropic thermal parameters.

give the triethylphosphine analogue $(OC)_4Mn(\mu-H)(\mu-SiPh_2)Pt(PEt_3)_2$ (**7**) (see Table I for spectroscopic data). In both phosphine and CO substitution reactions of **1** no trace of possible elimination products such as $Mn(CO)_5SiPh_2H$, $Mn(CO)_4(PR_3)H$, or $Pt(PR_3)_2(CO)_2$, etc. were observed.

Many transition-metal-silyl derivatives exhibit reactivity with a range of hydroxylic solvents.¹ During these reactions the M-Si bond may be cleaved (frequently generating a M-H bond and a silanol) or may remain intact. Complexes **1** are likewise reactive. Under mild and controlled reaction conditions (room temperature, a few hours, in toluene), hydroxylic nucleophiles (e.g., H_2O or $MeOH$) react with **1** to yield the μ -phosphido μ -hydrido bimetallic complex **8** (eq 7) (>90% from solution NMR data; ca. 50%



recrystallized yield; see Table I for spectroscopic data). The structure of **8** has been confirmed by X-ray crystallography (Figure 1). Apparently, the Si atom has been oxygenated and eliminated from the complex, presumably as $Ph_2Si(OMe)_2$ (from $MeOH$) or $Ph_2Si(OH)_2$ (from H_2O) (not isolated). There are numerous examples in the literature where a Ph group of a coordinated PPh_3 is cleaved and a μ -phosphido complex is formed.⁹ However, most usually require more vigorous reaction conditions than those reported here. Reactions involving P-Ph bond cleavage under equally mild conditions to the $\mathbf{1b} \rightarrow \mathbf{8}$

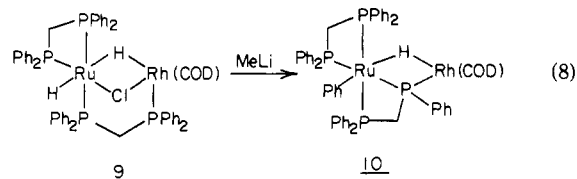
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Table II. Crystal Data, Details of Intensity Measurements, and Structure Refinements

| | |
|---|--|
| compd | $C_{40}H_{31}P_2PtMnO_4$ |
| system | monoclinic |
| $a \times b \times c$, Å | 12.929 (2) × 26.382 (5) × 11.245 (8) |
| β , deg | 110.52 (1) |
| U , Å ³ | 3592 |
| fw | 887.7 |
| Z/D_{calcd} , g cm ⁻³ | 4/1.63 |
| $F(000)$ | 1744 |
| μ (Mo K α), cm ⁻¹ | 43.7 |
| space group | $P2_1/c$ |
| T , °C | 23 |
| reflctns used in cell detmn | 25/(7.8 < θ < 16.0)° |
| diffractometer | Enraf-Nonius CAD4 |
| mode | $\omega:2\theta$ |
| wavelength | Mo K α radiation, $\lambda = 0.71069$ Å |
| scan ranges, ^a deg | 0.70 + 0.35 tan θ |
| max scan time, ^b s | 60 |
| max 2θ , deg | 52 |
| std reflns (no./interval, s) | 3/9000 |
| quadrants | $h, k, \pm l$ |
| no. of data colld ^c | 9272 |
| no. of nonzero data ^d | 6382 |
| struct soln ^e | Patterson (Pt + Mn), least-squares, Fourier, and ΔF Fourier |
| no. of data with $I \geq 3\sigma(I)$ | 4763 |
| R factors, R (wR) | 0.0348 (0.0460) |
| max shift/error | 0.30 |
| esdouv | 1.12 |
| weighting scheme ^f | $4F^2/[\sigma^2(I) + (0.06F^2)^2]$ |
| final diff Fourier max peaks, e Å ⁻³ | 1.07 (0.39, 0.12, 0.25), 1.06 Å from Pt; 1.03 (0.25, 0.15, 0.16), 0.86 Å from Pt; 0.96 (0.39, 0.16, 0.25), 0.99 Å from Pt; 0.91 (0.33, 0.17, 0.22), 0.83 Å from Pt |

^a Backgrounds by extending scan by 25% on either side of peak collected for half the time taken to collect peak. ^b Prescan at 10 deg min⁻¹, other scan speeds chosen to give $I/\sigma(I) \geq 25$ within the maximum scan time. ^c Includes 557 reflections remeasured due to a slight crystal movement during data collection. ^d Initial values of above 557 reflections and 1001 systematically absent or zero F_o reflections rejected. 1134 symmetry equivalent reflections then averaged ($R_{\text{merge}(I)} = 0.023$). ^e Hydrogen atoms on phenyl rings in calculated positions. Bridging hydrogen located in ΔF Fourier map and successfully refined in least squares. All non-H atoms with anisotropic thermal parameters (437 variables). ^f 10 reflections with bad $\omega\Delta F^2$ values and unsymmetrical backgrounds in data collection rejected from final cycles of least squares.

reaction (eq 7) include the formation of $[(PPh_3)PhPt(\mu-PPh_2)(\mu-H)Pt(PPh_3)_2]^+$ from the reaction of $Pt(COD)_2 + 2PPh_3$ with $[Pt(p\text{-tolyl})(\text{acetone})(PPh_3)_2]^+$ and H_2 at 0 °C.¹⁰ More recently the Ru-Rh bimetallic **9** has been shown to react with $MeLi$ with loss of methane to give a μ -phosphido μ -hydrido phenyl complex, **10**, under equally mild conditions¹¹ (eq 8). In the formation of both **8** and



10 an elimination under mild conditions $\{Ph_2Si(OH)_2$ for **8**; CH_4 for **10**\} presumably gives rise to coordinative unsaturation which is followed by cleavage of a Ph-P bond to give the observed phenyl μ -phosphido product. Al-

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Table III. Positional Parameters and Their Estimated Standard Deviations for Complex 8^c

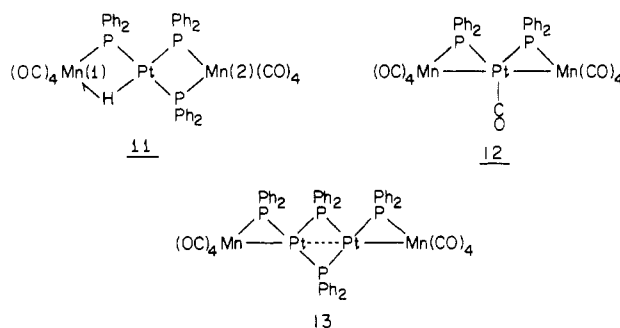
| atom | x | y | z | B, Å ² |
|------|-------------|-------------|-------------|-------------------|
| Pt | 0.31718 (2) | 0.14119 (1) | 0.20607 (2) | 3.052 (4) |
| Mn | 0.42436 (8) | 0.04685 (4) | 0.19873 (9) | 3.93 (2) |
| P1 | 0.1272 (1) | 0.13894 (6) | 0.1340 (1) | 3.18 (3) |
| P2 | 0.4994 (1) | 0.12463 (7) | 0.2760 (2) | 3.41 (3) |
| O1 | 0.6459 (5) | 0.0008 (3) | 0.2792 (6) | 8.0 (2) |
| O2 | 0.4161 (5) | 0.0759 (2) | -0.0598 (5) | 6.9 (2) |
| O3 | 0.2901 (5) | -0.0397 (2) | 0.0610 (6) | 8.0 (2) |
| O4 | 0.3857 (5) | 0.0156 (2) | 0.4349 (5) | 7.3 (2) |
| C1 | 0.5598 (6) | 0.0181 (3) | 0.2448 (7) | 5.5 (2) |
| C2 | 0.4217 (6) | 0.0659 (3) | 0.0405 (7) | 4.9 (2) |
| C3 | 0.3417 (6) | -0.0057 (3) | 0.1183 (7) | 5.3 (2) |
| C4 | 0.4049 (6) | 0.0287 (3) | 0.3485 (7) | 5.2 (2) |
| C11 | 0.3261 (4) | 0.2183 (2) | 0.2257 (5) | 3.3 (1) |
| C12 | 0.3688 (5) | 0.2437 (3) | 0.3400 (6) | 4.1 (2) |
| C13 | 0.3726 (6) | 0.2962 (3) | 0.3462 (7) | 5.5 (2) |
| C14 | 0.3348 (6) | 0.3245 (3) | 0.2365 (7) | 5.6 (2) |
| C15 | 0.2928 (6) | 0.3004 (3) | 0.1226 (7) | 5.4 (2) |
| C16 | 0.2893 (5) | 0.2480 (3) | 0.1170 (6) | 4.4 (2) |
| C111 | 0.0745 (5) | 0.0997 (3) | -0.0077 (5) | 3.7 (1) |
| C112 | 0.1327 (6) | 0.1020 (3) | -0.0902 (7) | 5.5 (2) |
| C113 | 0.0963 (8) | 0.0726 (4) | -0.2002 (7) | 7.8 (3) |
| C114 | 0.0082 (8) | 0.0414 (3) | -0.2254 (7) | 6.9 (3) |
| C115 | -0.0493 (8) | 0.0403 (3) | -0.1446 (7) | 6.5 (2) |
| C116 | -0.0166 (6) | 0.0682 (3) | -0.0369 (7) | 5.1 (2) |
| C121 | 0.0499 (5) | 0.1979 (3) | 0.0901 (6) | 3.6 (1) |
| C122 | -0.0177 (6) | 0.2081 (3) | -0.0333 (7) | 5.5 (2) |
| C123 | -0.0656 (7) | 0.2559 (4) | -0.0623 (8) | 7.1 (2) |
| C124 | -0.0471 (7) | 0.2921 (3) | 0.0285 (9) | 7.2 (2) |
| C125 | 0.0164 (7) | 0.2811 (3) | 0.1496 (8) | 6.9 (2) |
| C126 | 0.0663 (6) | 0.2350 (3) | 0.1826 (7) | 4.9 (2) |
| C131 | 0.0745 (5) | 0.1116 (3) | 0.2514 (5) | 3.4 (1) |
| C132 | 0.1478 (5) | 0.0881 (3) | 0.3587 (6) | 4.3 (2) |
| C133 | 0.1065 (7) | 0.0688 (3) | 0.4465 (7) | 5.9 (2) |
| C134 | -0.0018 (6) | 0.0709 (3) | 0.4305 (7) | 5.9 (2) |
| C135 | -0.0730 (6) | 0.0934 (4) | 0.3269 (7) | 6.0 (2) |
| C136 | -0.0369 (6) | 0.1148 (3) | 0.2350 (6) | 5.3 (2) |
| C211 | 0.5769 (5) | 0.1284 (3) | 0.4451 (6) | 4.0 (2) |
| C212 | 0.5236 (6) | 0.1279 (3) | 0.5315 (7) | 4.8 (2) |
| C213 | 0.5820 (6) | 0.1254 (4) | 0.6607 (7) | 5.6 (2) |
| C214 | 0.6951 (7) | 0.1236 (4) | 0.7028 (7) | 6.2 (2) |
| C215 | 0.7504 (6) | 0.1248 (4) | 0.6205 (7) | 6.0 (2) |
| C216 | 0.6909 (6) | 0.1270 (3) | 0.4917 (6) | 5.0 (2) |
| C221 | 0.5845 (5) | 0.1582 (3) | 0.2016 (6) | 3.9 (1) |
| C222 | 0.6343 (6) | 0.1333 (3) | 0.1289 (7) | 5.2 (2) |
| C223 | 0.6909 (6) | 0.1616 (4) | 0.0644 (7) | 6.1 (2) |
| C224 | 0.6975 (6) | 0.2116 (4) | 0.0744 (8) | 6.9 (2) |
| C225 | 0.6465 (7) | 0.2370 (4) | 0.1456 (9) | 7.1 (3) |
| C226 | 0.5909 (6) | 0.2097 (3) | 0.2092 (8) | 5.7 (2) |
| H(μ) | 0.297 (5) | 0.081 (3) | 0.173 (7) | 8 (2)* |

^aThe parameter with an asterisk was refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)$.

though 8 is isolated in reasonable yield, trace amounts of $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{H}^{12}$ and a small amount of an ill-defined material are always observed. Formation of these minor products is minimized by the use of a limited amount of methanol or water (between 3-fold and 10-fold excess). When the triethylphosphine complex 7 was reacted with methanol, no $\mu\text{-PET}_2$ species was detected. Instead a large amount of $\text{Mn}(\text{CO})_4(\text{PET}_3)\text{H}^{12}$ and a quantity of an ill-defined red material were isolated.

Molecular Structure of $(\text{OC})_4\text{Mn}(\mu\text{-PPh}_2)(\mu\text{-H})\text{PtPh}(\text{PPh}_3)$ (8). An ORTEP drawing of 8 giving the atom-labeling scheme is shown in Figure 1. Crystallographic data, final atomic positional parameters, and relevant bond angles and distances are given in Tables II–IV. The molecular structure of 8 consists of edge-

shared pseudooctahedral Mn and pseudo-square-planar Pt centers linked by a planar MnPt bridging unit. The coordination geometry at platinum is very similar to that of the phenylplatinum moiety in $[(\text{PPh}_3)_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-H})\text{PtPh}(\text{PPh}_3)]^+$.¹⁰ In the “ $\text{Mn}(\mu\text{-PPh}_2)(\mu\text{-H})\text{Pt}$ ” unit the μ -phosphido ligand exhibits an acute $\angle\text{MnPtP}$ of 78° , and the MnPt separation of $2.864(1) \text{ \AA}$ is within the range expected for a MnPt bond.¹³ However, the question of whether this distance necessarily implies a *direct* metal–metal bond is open to question. Several studies have concluded that metal–metal bonding in some doubly bridged binuclear systems are better discussed in terms of multicentered linkages between the metals and the bridging groups,¹⁴ and it seems more likely that the MnPt separation in 8 is more a consequence of the bonding requirements of the bridging ligands. The MnPt separation is comparable to that observed for $\text{Mn}(1)\text{Pt}$ in 11 $\{2.847(2) \text{ \AA}\}$ containing a “ $\text{Mn}(\mu\text{-PPh}_2)(\mu\text{-H})\text{Pt}$ ” unit and significantly longer than the MnPt separations in 12 and 13 $\{2.741(1) \text{ and } 2.717(2) \text{ \AA}\}$, complexes which contain a bent MnPt bond and a single bridging ligand.^{15,16} In 8 the $\text{Pt}\text{-}\mu\text{-P}$ distance of $2.248(2) \text{ \AA}$ is comparable to that observed in $[(\text{Ph}_3\text{P})_2\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-H})\text{Re}(\text{NO})(\text{Cp})]\text{BF}_4$ of $2.255(2) \text{ \AA}$.¹⁷ Both of these distances are, however, significantly shorter than the $\text{Pt}\text{-P}$ distances observed in several other compounds containing PtMn triangular units (cf. 11,¹⁵ 12,¹⁶ and 13¹⁵) where the $\text{Pt}\text{-}\mu\text{-P}$ distances



are generally ca. $2.27\text{--}2.31 \text{ \AA}$.^{13a} In 8 the three-center, two-electron hydride bridge is fairly symmetrical with a $\angle\text{Pt}\text{-H}\text{-Mn}$ angle of $113(4)^\circ$, and there is relatively good agreement with other observed $\text{Pt}\text{-H}$ and $\text{Mn}\text{-H}$ distances (Table V). Completing the coordination of the Pt is a phenyl group trans to the hydride bridge with a normal $\text{Pt}\text{-C}(\text{sp}^2)$ distance of $2.045(6) \text{ \AA}$ and a PPh_3 group with a $\text{Pt}\text{-P}$ distance of $2.301(2) \text{ \AA}$.

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Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) in the Molecular Structure of 8

| bond lengths | | | bond angles | | | | | | | |
|--------------|--------|-----------|-------------|--------|--------|------------|--------|--------|--------|-----------|
| atom 1 | atom 2 | dist | atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
| Pt | Mn | 2.864 (1) | Mn | Pt | P1 | 115.75 (5) | C1 | Mn | H1 | 172 (3) |
| Pt | P1 | 2.301 (2) | Mn | Pt | P2 | 51.93 (5) | C2 | Mn | C3 | 85.2 (4) |
| Pt | P2 | 2.248 (2) | Mn | Pt | C11 | 149.1 (2) | C2 | Mn | C4 | 171.7 (3) |
| Pt | C11 | 2.045 (6) | Mn | Pt | H1 | 35 (3) | C2 | Mn | H1 | 90 (2) |
| Pt | H1 | 1.64 (8) | P1 | Pt | P2 | 167.31 (7) | C3 | Mn | C4 | 90.7 (4) |
| Mn | P2 | 2.306 (2) | P1 | Pt | C11 | 94.4 (2) | C3 | Mn | H1 | 87 (3) |
| Mn | C1 | 1.809 (8) | P1 | Pt | H1 | 80 (3) | C4 | Mn | H1 | 82 (2) |
| Mn | C2 | 1.830 (8) | P2 | Pt | C11 | 98.2 (2) | Pt | P1 | C111 | 110.4 (2) |
| Mn | C3 | 1.791 (8) | P2 | Pt | H1 | 87 (3) | Pt | P1 | C121 | 119.3 (2) |
| Mn | C4 | 1.851 (9) | C11 | Pt | H1 | 173 (3) | Pt | P1 | C131 | 112.1 (2) |
| Mn | H1 | 1.80 (8) | Pt | Mn | P2 | 50.14 (4) | C111 | Pt1 | C121 | 104.3 (3) |
| P1 | C111 | 1.820 (7) | Pt | Mn | C1 | 141.8 (3) | C111 | P1 | C131 | 106.7 (3) |
| P1 | C121 | 1.822 (6) | Pt | Mn | C2 | 86.9 (2) | C121 | P1 | C131 | 103.0 (3) |
| P1 | C131 | 1.833 (6) | Pt | Mn | C3 | 118.7 (3) | Pt | P2 | Mn | 77.93 (6) |
| P2 | C211 | 1.816 (7) | Pt | Mn | C4 | 88.7 (3) | Pt | P2 | C211 | 118.8 (2) |
| P2 | C221 | 1.827 (7) | Pt | Mn | H1 | 32 (3) | Pt | P2 | C221 | 118.1 (2) |
| O1 | C1 | 1.138 (9) | P2 | Mn | C1 | 91.7 (3) | Mn | P2 | C211 | 116.6 (2) |
| O2 | C2 | 1.136 (9) | P2 | Mn | C2 | 89.1 (3) | Mn | P2 | C221 | 120.0 (2) |
| O3 | C3 | 1.167 (9) | P2 | Mn | C3 | 167.8 (3) | C211 | P2 | C221 | 104.7 (3) |
| O4 | C4 | 1.139 (9) | P2 | Mn | C4 | 93.5 (3) | Mn | C1 | O1 | 176.9 (7) |
| | | | P2 | Mn | H1 | 82 (3) | Mn | C2 | O2 | 176.7 (7) |
| | | | C1 | Mn | C2 | 94.6 (4) | Mn | C3 | O3 | 176.5 (8) |
| | | | C1 | Mn | C3 | 99.5 (4) | Mn | C4 | O4 | 174.6 (8) |
| | | | C1 | Mn | C4 | 93.3 (3) | | | | |

Table V. Some Observed Pt-H and Mn-H Bond Distances (Å)

| compd | distance(s) | comments |
|--|--|---|
| (OC) ₄ Mn(μ-H)(μ-PPH ₂)PtPh(PPh ₃) (8) | 1.64 (8) (Pt-H), 1.80 (8) (Mn-H) [Pt-H-Mn = 113 (4)°] | X-ray, least squares refined |
| [Cp(ON)Re(μ-H)(μ-PPH ₂)Pt(PPh ₃) ₂] [†] ^b | 2.21 (6) (Pt-H), 1.57 (6) (Re-H) [Pt-H-Re = 97 (3)°] | X-ray, least-squares refined, BF ₄ ⁻ salt |
| [(dippe)Pt ¹ (μ-H ¹)(μ-H ²)Pt ² (H)(dippe)] [†] (triclinic) ^c | 1.610 (2) (Pt ¹ -H ¹), 1.860 (2) (Pt ² -H ²), 2.049 (2) (Pt ¹ -H ²), 1.691 (2) (Pt ² -H ²), 1.656 (2) (Pt ² -H) [Pt-H-Pt = 99.4 (1), 93.4 | neutron diffn, BPh ₄ ⁻ salt |
| [(dippe)Pt ¹ (μ-H ¹)(μ-H ²)Pt ² (H)(dippe)] [†] (monoclinic) ^d | 1.53 (Pt-H ₁), 1.78 (Pt ¹ -H ¹), 2.05 (Pt ¹ -H ²), 1.40 (Pt ² -H ²), 1.71 (Pt ² -H ²) [Pt-H-Pt = 93, 117°] | X-ray, H atoms from ΔF map, not refined, BPh ₄ ⁻ salt |
| [(dippe)Pt(μ-H)(μ-CO)Pt(dippe)] [†] ^e | 1.55 (4) (Pt-H) [Pt-H-Pt = 122 (2)°] | X-ray, C ₂ mol sym, least-squares refined, BF ₄ ⁻ salt |
| (Et ₃ P) ₂ Pt(H)B ₉ H ₁₀ S ^f | 1.66 (Pt-H) | X-ray, H atom from ΔF map |
| Pt(H)(PPh ₃) ₂ (C≡CC(OH)MeEt) ^g | 1.98 (Pt-H) | X-ray, H atom from ΔF map |
| [PtH(μSiMe ₂)(PCx ₃) ₂] ^h | 1.78 (Pt-H), 1.72 (Si-H) [Pt-H-Si = 87.6°] | X-ray, H atom from ΔF map |
| (⁷⁵ CH ₃ C ₅ H ₄)Mn(CO) ₂ (H)SiFPh ₂ ⁱ | 1.569 (4) (Mn-H), 1.802 (5) (SiH) [Mn-H-Si = 88.2 (2)] | neutron diffn |
| HMn(CO) ₅ ^j | 1.601 (16) | neutron diffn |
| H ₃ Mn ₃ (CO) ₁₂ ^k | 1.61 (13), 1.64 (13), 1.79 (12), 1.79 (11), 1.71 (11), 1.78 (13) [Mn-H-Mn = 119 (6), 126 (7), 149 (9)] | X-ray, least-squares refined |
| (CO) ₃ Mn(B ₉ H ₁₀) ^l | 1.68 (4), 1.81 (3) (×2) | X-ray, least squares refined |
| (CO) ₃ Mn(B ₉ H ₁₂ OC ₄ H ₈) ^m | 1.75 (4) | X-ray, least squares refined |
| HMn(CO) ₅ ⁿ | 1.58 (2) | el diffn |
| (CO) ₃ MnB ₃ H ₈ ^o | 1.69 (5), 1.75 (4), 1.64 (4) | X-ray, least squares refined |

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The (OC)₄Mn(μ-PR₂) unit" has now been structurally characterized in a range of bimetallic systems (Table VI). For complexes 11 and [Mn(μ-PH₂)(CO)₄]₂ which contain "Mn(μ-PR₂)₂M" units with no metal-metal bond, the Mn-μ-P bond length is in the range 2.35-2.38 Å. For 8, 11, and (OC)₄Mn(μ-H)(μ-PPH₂)Mn(CO)₄ the Mn-μ-P bond lengths associated with a "Mn(μ-H)(μ-PR₂)M" unit are 2.306 (2), 2.306 (4), and 2.284 (6) Å, respectively. In 12, 13, and (OC)₄Mn(μ-PPH₂)Fe(CO)₄, systems containing metal-metal bonded "Mn(μ-PPH₂)M" units, the Mn-μ-P bond lengths are 2.241 (3)/2.237 (2), 2.242 (4), and 2.257 (6) Å, respectively. Thus the decrease in the metal-metal separation as one goes from "Mn(μ-PPH₂)₂M" (no MnM

bond) to "Mn(μ-PPH₂)(μ-H)M" to "Mn(μ-PPH₂)M" results in a narrowing of the ∠MnPM' angle and a slight but significant shortening of 0.08-0.12 Å in the Mn-P bond length. A similar shortening of the M-μ-P bond is observed on going from (OC)₄M(μ-PR₂)₂M'CP₂ (M = Mo, M' = Hf, R = Et; M = W, M' = Zr, R = Ph) {no or only very weak metal-metal bonds^{23,24} to the metal-metal bonded systems (OC)₄M(μ-PPH₂)₂Pt(PR₃) (M = Mo, W)^{25,26} and

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Table VI. Selected Bond Length (Å) and Bond Angle (deg) Data for a Series of μ -Phosphido-Bridged Mn-M' (M' = Pt) Systems and Closely Related Analogues

| compound | M' | Mn-M' bonding | Mn-M' sepn | Mn-P(μ) | Pt-P(μ) | \angle MnPM' |
|---|----|---------------|------------------------|------------------------|---------------|------------------------|
| 8 | Pt | μ -H | 2.864 (1) | 2.306 (2) | 2.248 (2) | 77.9 (1) |
| 11 {Mn(1) data} ¹⁵ | Pt | μ -H | 2.847 (2) | 2.306 (4) | 2.273 (4) | 76.9 (2) |
| 12 ¹⁶ | Pt | Mn-Pt | 2.741 (1) | 2.241 (3) | 2.319 (3) | 74.0 (1) |
| | | | 2.747 (2) | 2.237 (2) | 2.305 (2) | 74.3 (1) |
| 13 ¹⁵ | Pt | Mn-Pt | 2.717 (1) | 2.242 (4) | 2.265 (3) | 74.1 (1) |
| 11 {Mn(2) data} ¹⁵ | Pt | none | 3.618 (2) | 2.379 (4) | 2.299 (4) | 101.2 (1) |
| | | | | 2.355 (4) | 2.325 (4) | 101.3 (1) |
| [Mn(μ -PH ₂)(CO) ₄] ₂ ¹⁹ | Mn | none | 3.703 (1) | 2.351 (2) ^a | | 103.9 (1) ^a |
| [Mn(μ -PH ₂)(CO) ₄] ₃ ¹⁹ | Mn | none | 4.330 (1) ^a | 2.383 (1) ^a | | 130.0 (1) ^a |
| [(CO) ₄ Mn(μ -PPh ₂)Fe(CO) ₄] ₂ ²⁰ | Fe | Mn-Fe | 2.825 (5) | 2.257 (6) | | 77.8 (2) |
| [(CO) ₄ Mn(μ -PPh ₂)(μ -H)Mn(CO) ₄] ₂ ¹⁸ | Mn | μ -H | 2.937 (5) | 2.284 (6) | | 80.0 (1) |

^a Average.

(OC)₄W(μ -PPh₂)₂IrH(CO)(PPh₃).²⁷ Likewise on going from (OC)₅W(μ -PPh₂)OsH(CO)₂(PPh₂Me)(PPh₂H)²⁸ to

(OC)₄W(μ -PPh₂)(μ -PPh₂CH(OMe))Os(CO)₂(PMe₂Ph)²⁹ W- μ -PPh₂ decreases from 2.623 (2) to 2.538 (3) Å and Os- μ -PPh₂ decreases from 2.478 (2) to 2.357 (7) Å, respectively. This consistent shortening of M-P(μ) bond length as the \angle MnPM' angle becomes more acute is comparable to the decrease in P-P from a normal value of 2.27 Å to a value of 2.20 Å in the "strained" molecule P₄. The shorter bond length in P₄ has been ascribed to "bent" P-P σ bonding.³⁰ We propose that *the shortening of the Mn- μ -P bond length on going from no-metal-metal bond to metal-metal bonded systems can likewise be ascribed to ring strain effects and bent M-P σ bonding as the \angle MnPM' bond angle is reduced.* Some support for this hypothesis is the observation that the large deviations of \angle PtPt angles from 90° or 180° ideal values in "planar" PtXY(PR₃)₂ complexes have recently been rationalized reasonably successfully in terms of bent P-Pt σ bonds.³¹ An assumption that M-P bonds are fairly easily bent (without rehybridization at P) also accounts for the fact that the \angle CPC angles of "strained" μ -PR₂ groups (\angle MnPM = 70–80°) are similar to \angle CPC angles in unstrained μ -PR₂ groups and coordinated PR₃ ligands (typically 102–108°; \angle C-P- μ -C = 104.7 (3)° in 8).

The metal-ligand bond distances and structural features of 8 are consistent with the Mn^(II)Pt^(III) valence-bond representations A and/or B, as are the IR data for 8 which

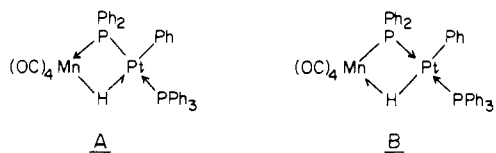


exhibit ν (CO) bands at frequencies comparable to those observed for (OC)₄MnH(PPh₃).¹² The observed $J_{195\text{Pt}-1\text{H}}$ value of 370 Hz for the μ -hydrido ligand of 8 is notably low when compared with values of ca. 660 Hz for the μ -hydrido ligand of (CO)₄M(μ -H)(μ -PPh₂)Pt(PPh₃)₂ (M = Cr, Mo, W)⁶ and 520 Hz for (OC)₃Fe(μ -H)(μ -PCy₂)Pt(PET₃)₂.³² The low $J_{195\text{Pt}-1\text{H}}$ value is consistent with the

expected high trans influence of the phenyl group and suggests a rather weak μ -H-Pt bond.

In conclusion the two-electron oxidative addition of a Si-H bond of a coordinated silyl ligand provides a simple route into μ -silylene systems. The reaction probably proceeds in a similar manner to that observed for complexed secondary phosphine analogues.

Experimental Section

All reactions were carried out by using dry and oxygen-free conditions. Complexes Mn(CO)₅SiR₂H (R = Me, Ph, and Cl),^{4,5} Pt(C₂H₄)(PPh₃)₂, and Pt(PPh₃)₄³³ were synthesized according to the literature methods. NMR spectra were recorded on a Varian XL-200 spectrometer. Solution infrared spectra were recorded on a Nicolet 10DX-FTIR using KBr cells with 0.1 mm pathlength. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Vancouver, Canada. Spectroscopic and analytical data are given in Table I.

(OC)₄Mn(μ -SiR₂)(μ -H)Pt(PPh₃)₂ (1). In a typical reaction a mixture of Pt(C₂H₄)(PPh₃)₂ (0.20 g, 0.27 mmol) and the appropriate amount of Mn(CO)₅SiR₂H (0.27 mmol) were stirred at room temperature in 15 mL of toluene. The reactions were monitored by IR until bands due to Mn(CO)₅SiR₂H disappeared (1a and 1b, 1–2 h; 1c, 1 h). When the solution was concentrated to 5 mL, yellow crystalline products formed which were separated by filtration and dried. See Table I for analytical and spectroscopic data.

(OC)₄Mn(μ -SiPh₂)(μ -H)Pt(PET₃)₂ (7). To a suspension of 1b (0.100 g, 0.093 mmol) in hexane (20 mL) was added a stoichiometric amount of PET₃ (0.023 g, 0.19 mmol). The reaction mixture was stirred at room temperature for 5 h. The hexane was decanted off, and the resultant solid was washed with more hexane and dried. The product was characterized as 7 via IR and NMR spectroscopy (see Table I).

Reaction of 1b with Carbon Monoxide. Carbon monoxide was bubbled into a suspension of 1b (0.10 g) in hexanes for 30 min to give an off-white solid. The solvent was decanted and washed several times with hexanes (to remove PPh₃) and then dried under 1 atm of N₂. The product was identified as 6 by IR and NMR (Table I).

Reactions of 1a,b with Methanol. Methanol (80 μ L, 8-fold excess) was added to a benzene solution (10 mL) of 1 (ca. 0.050 g) and the reaction stirred at room temperature and monitored by IR until the ν (CO) bands of 1 disappeared (1a, \approx 5 h; 1b, \approx 8 h). A red solution forms in all cases, but on standing overnight yellow crystals of the product 8 were isolated and structurally characterized by IR and NMR spectroscopy (Table I) and X-ray crystallography.

X-ray Crystallography. Orange crystals of complex 8 were not well-formed. A somewhat irregular block with poorly formed faces of overall dimensions 0.275 \times 0.200 \times 0.200 mm was eventually chosen and used throughout. Precession photographs were used to check crystal quality and further work on the diffractometer gave the crystal data summarized in Table II which also contains details of the data collection options used. Lorentz

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and polarization corrections were applied to all data collected. Since it was not possible to confidently assign crystal faces, no absorption correction was attempted. In view of the fairly regular shape and relatively small value of μ this is not considered to be a major source of error and the low merging R factor for averaging 1134 symmetry-equivalent data is consistent with this observation. The structure was solved as indicated. In the final cycles of least squares hydrogen atoms on the phenyl rings were placed in calculated positions. A subsequent ΔF Fourier map contained a peak at (0.277, 0.066, 0.125) of reasonable height which was in a chemically sensible position to be the H-atom bridging Pt and Mn. Least squares refinement of this atom produced no drastic shifts in its position. Full-matrix least squares refinements minimizing $\sum w\Delta F^2$ then converged to the indicated residuals. No extinction corrections were considered necessary. In the refinements programs of the Enraf-Nonius SDP system on a PDP 11/23 computer were used throughout. The final atomic positional

parameters are given in Table III, and selected bond lengths and bond angles are given in Table IV.

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Registry No. 1a, 118398-33-7; 1b, 118398-34-8; 1c, 118398-35-9; 6, 118417-94-0; 7, 118398-36-0; 8, 118398-37-1; Mn(CO)₅SiMe₂H, 118398-31-5; Mn(CO)₅SiPh₂H, 118398-32-6; Mn(CO)₅SiCl₂H, 20347-38-0; Pt(C₂H₄)(PPh₃)₂, 12120-15-9; Pt(PPh₃)₄, 14221-02-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen atom positional parameters, and bond lengths and angles for 8 (5 pages); a listing of final structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

Synthesis, Reactivity and Kinetic Studies of Bis(η^5 -cyclopentadienyl)titanium Methylidene Phosphine Complexes

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Syntheses of several bis(η^5 -cyclopentadienyl)titanium methylidene phosphine complexes are reported. The titanocene methylidene phosphine complexes are generated from thermolysis of titanocene metallacyclobutanes in the presence of excess phosphine. Spectral data and reactivity are consistent with a methylidene phosphine complex rather than an ylide complex. The titanocene methylidene phosphine complexes react with olefins to form metallacyclobutanes, alkynes to form metallacyclobutenes, and CO to form a ketene complex. The phosphine ligand is labile, and an equilibrium mixture is rapidly established if a second phosphine is added. The kinetics of this equilibration and the kinetics of the reaction of titanocene methylidene phosphine complexes with alkynes and olefins are reported. The reactions proceed by rate-determining loss of phosphine followed by rapid trapping of titanocene methylidene.

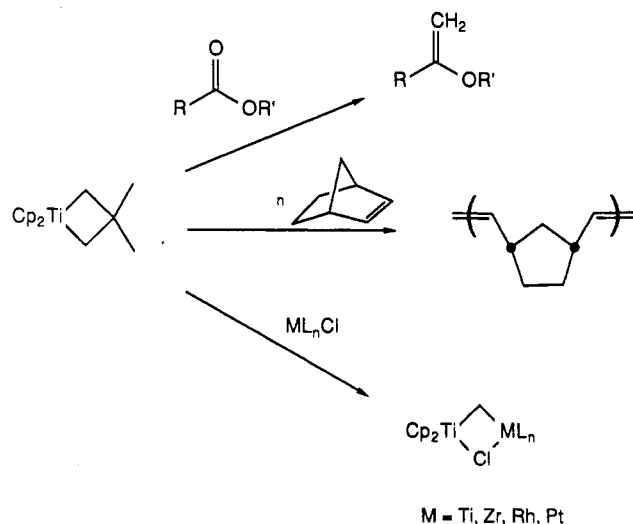
Introduction

Metal alkylidene complexes have been implicated as intermediates in many important reactions, including alkene metathesis,¹ alkene² and alkyne polymerization,³ cyclopropanation of olefins,⁴ and methylenation of carbonyl compounds.⁵ Surface-bound alkylidenes have been postulated to be intermediates in Fischer-Tropsch chemistry.⁶ As models for these and other reactions, several bimetallic bridging methylidene compounds have been synthesized and studied.⁷ Many carbene complexes containing heteroatom substituents have also been synthesized; their chemistry is quite different from methylidene complexes of the early transition metals⁸ and other terminal methylene complexes.⁹⁻¹²

Titanocene dichloride and trimethylaluminum¹³ react to yield a stable, soluble dimethylaluminum chloride-titanocene methylidene complex (Tebbe's reagent, 1).¹⁴ The Tebbe reagent is an olefin metathesis catalyst, readily methylenates carbonyl compounds, and serves as a precursor to other methylidene derivatives.¹⁵ A titanocene methylidene species has been implicated as the active species in many of these reactions.

Titanacyclobutanes can be isolated from the reaction of 1 with olefins in the presence of Lewis bases.¹⁶ Tita-

Scheme I. Reactivity of Titanocene Metallacyclobutanes



nacyclobutanes transfer methylene groups to carbonyl functionalities,⁵ ring-open polymerize strained cyclic ole-

[†] Contribution No. 7738.

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