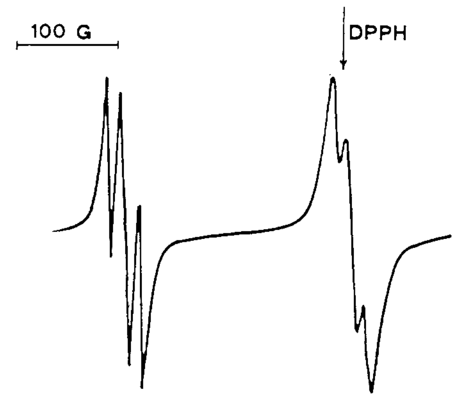

Figure 2. X-band ESR spectrum of $[(np_3)RhC{\equiv}CPh]BPh_4$ in THF at 298 K.

which is typical of TBP np_3 complexes of rhodium(I).[5,7] Furthermore, the resonance of the vinylidene proton (a doublet of quartets) clearly indicates coupling to three equivalent phosphorus nuclei [$^4J(HP) = 13.8$ Hz] and the rhodium atom [$^3J(HRh) = 1.1$ Hz]. Compound **1** is stable for hours at room temperature in deaerated THF solutions from which it can be recrystallized by addition of ethanol. In contrast, **1** decomposes within minutes under nitrogen in refluxing THF to give a yellow-green solution from which a microcrystalline solid of formula $[(np_3)RhC{\equiv}CPh]BPh_4$[8] (**4**) can be obtained by addition of $NaBPh_4$ (yield 75%). Dihydrogen is evolved almost quantitatively during the thermal decomposition of **1** (determined by GC). Compound **4**, which still contains a σ-bonded acetylide ligand [$\nu(C{\equiv}C) = 2115$ cm^{-1}], is paramagnetic with a magnetic moment corresponding to one unpaired spin ($\mu_{eff} = 1.90\ \mu_B$). Alternatively, **4** can be synthesized by both chemical[8] and electrochemical oxidation of the σ-acetylide complex **2**. Figure 1 shows a cyclic voltammogram of **2** in THF. Analysis of the CV responses together with results from controlled potential coulometry indicate that two one-electron quasi-reversible processes can be attributed to the sequence $Rh(I) \rightleftharpoons Rh(II) \rightleftharpoons Rh(III)$ at $E^{\circ\prime} = -0.45$ V and $E^{\circ\prime} = +0.02$ V, respectively. Exhaustive one-electron electrolysis at -0.3 V affords a greenish solution from which the paramagnetic complex **4** can be obtained after solvent evaporation.

The X-band ESR spectra of **4** in the solid state and frozen solution (THF, 100 K) are essentially coincident. These can be modeled by using a $S = {}^1/_2$ spin Hamiltonian with $g_{\parallel} = 2.007$ ($A_{\parallel} = 250$ G) and $g_{\perp} = 2.082$ ($A_{\perp} = 201$ G). A three-line resolution with $A = 18$ G is present in each perpendicular absorption. The pattern $g_{\perp} > g_{\parallel} \simeq 2.00$ strongly indicates that the complex exhibits square-pyramidal (SQ) symmetry with the unpaired electron in the dz^2 orbital.[9] It is therefore reasonable to consider the large A values[10] as originated by coupling of the unpaired electron to the apical phosphorus while the splitting observed in the perpendicular absorptions is assigned to interaction with the two basal phosphorus atoms. The room-temperature ESR spectrum of **4** in THF solution at 298 K (Figure 2) consists of a doublet of triplets centered at $\langle g \rangle = 2.062$. The spectrum has been perfectly simulated[11] by considering the following parameters: $\langle A_1 \rangle = 222$ G, $\langle A_2 \rangle = 21$ G, and $\langle A_3 \rangle = 14$ G. The largest value, $\langle A_1 \rangle$, is assigned to coupling of the unpaired electron to the apical phosphorus nucleus as expected for a phosphorus looking at a dz^2 SOMO. The different and relatively small couplings to the two equatoral phosphorus nuclei are consistent with some distortion in the SQ coordination polyhedron. In summary, the spectrum can be described as a doublet of two pseudotriplets, each of which results from the sum of two doublets.

The dicationic complex of rhodium(III) $[(np_3)RhC{\equiv}CPh](BF_4)_2$ (**5**) is prepared as yellow crystals by adding 1 or two equiv of $AgBF_4$ to THF solutions of **4** and **2**, respectively (yield ca 80%).[13] The compound displays in THF a cyclic voltammogram complementary to that shown by **2**; i.e., the two one-electron redox changes now correspond to the sequential cathodic processes Rh(III)/Rh(II) and Rh(II)/Rh(I). On the basis of $^{31}P\{^1H\}$ NMR data, **5** is assigned a SQ structure (AM_2X spin system), therefore confirming the reliability of the ESR technique in establishing the structure of the oxidized congener **4**.

Registry No. **1**, 114580-94-8; **2**, 114580-95-9; **3**, 85233-91-6; **4**, 114580-97-1; **5**, 114580-99-3.

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[8] One equivalent of solid $AgBF_4$ was added portionwise to a THF solution of **2** under nitrogen. The solution becomes greenish and separates **4** after addition of $NaBPh_4$; yield 65%. Anal. Calcd (Found): C, 75.52 (75.22); H, 5.73 (5.99); N, 1.19 (1.07); Rh, 8.74 (8.58). IR (Nujol): $\nu(C{\equiv}C)$ 2115 (w), phenyl-reinforced vibration 1590 cm^{-1}.

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[11] The different line widths (5 G) of the two largely separated signals is due to the line-width dependence on the m_I value.[12]

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[13] Anal. Calcd (Found): C, 58.06 (58.23); H, 4.68 (4.59); N, 1.21 (1.36); Rh, 9.85 (9.98). IR (Nujol): $\nu(C{\equiv}C)$ 2125 (m), phenyl-reinforced vibration 1600 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 213 K): AM_2X pattern, $\delta(P_A)$ 33.71 [$J(P_AP_M) = 22.6$ Hz, $J(P_ARh) = 129.3$ Hz], $\delta(P_M)$ 23.43 [$J(P_MRh) = 90.4$ Hz]. At variance with **1** which is fluxional, the ethylenic chains of np_3 are not equivalent in **5** and give rise to a very complicated ^1H NMR pattern.

Intramolecular Activation of a C–H Bond in a CH_3–Si Group by Manganese. The Crystal and Molecular Structure of $(OC)_3Mn{-}CH_2Si(CH_3)(CH_2P(C_6H_5)_2)_2$

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Summary: Activation of a C–H bond in a CH_3–Si group by manganese has been observed in the thermal reaction between $CH_3Mn(CO)_5$ and $(C_6H_5)_2PCH_2Si(CH_3)_2CH_2P(C_6H_5)_2$. The crystal and molecular structure of the product of the reaction, $(OC)_3Mn{-}CH_2Si(CH_3)(CH_2P(C_6H_5)_2)_2$, is reported.

The list of organometallic transition-metal complexes known to activate C–H bonds of alkanes continues to lengthen as new and often unexpected discoveries are made.[2,3] This paper reports the serendipitous discovery

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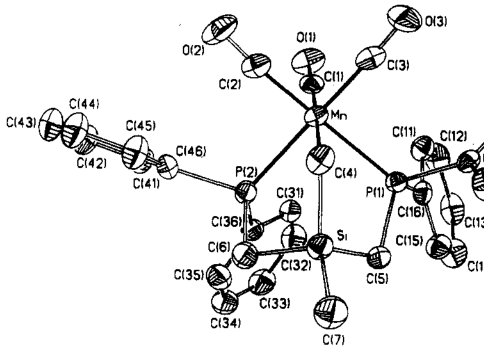


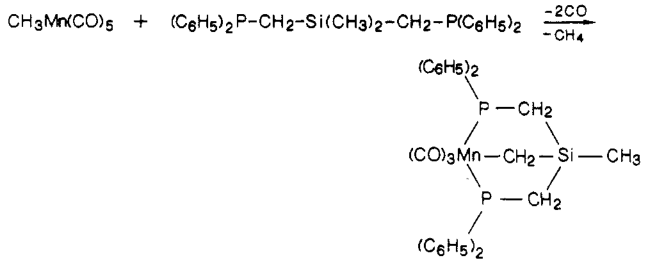
Figure 1. Molecular structure and labeling scheme for $C_{31}H_{29}O_3MnP_2Si$ (2) with 40% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Mn–P(1), 2.344 (1); Mn–P(2), 2.363 (1); Mn–C(1), 1.798 (4); Mn–C(2), 1.799 (5); Mn–C(3), 1.803 (5); Mn–C(4), 2.198 (5); P(1)–C(5), 1.812 (5); P(1)–C(16), 1.838 (3); P(1)–C(26), 1.845 (3); P(2)–C(6), 1.830 (5); P(2)–C(36), 1.835 (3); P(2)–C(46), 1.841 (3); Si–C(4), 1.843 (5); Si–C(5), 1.897 (5); Si–C(6), 1.870 (5); Si–C(7), 1.872 (5); O(1)–C(1), 1.154 (6); O(2)–C(2), 1.152 (6); O(3)–C(3), 1.148 (6); P(1)–Mn–P(2), 92.6 (1); P(1)–Mn–C(1), 100.2 (1); P(1)–Mn–C(2), 168.3 (2); P(1)–Mn–C(3), 88.1 (1); P(1)–Mn–C(4), 80.9 (1); P(2)–Mn–C(1), 94.4 (1); P(2)–Mn–C(2), 90.8 (2); P(2)–Mn–C(3), 174.0 (2); P(2)–Mn–C(4), 85.4 (1); C(1)–Mn–C(2), 90.7 (2); C(1)–Mn–C(3), 91.3 (2); C(1)–Mn–C(4), 178.9 (2); C(5)–P(1)–C(26), 103.2 (2); Mn–P(2)–C(6), 110.1 (2); Mn–P(2)–C(36), 121.0 (1); Mn–P(2)–C(46), 114.9 (1), C(6)–P(2)–C(36), 103.4 (2); C(6)–P(2)–C(46), 103.9 (2); C(4)–Si–C(5), 106.9 (2); C(4)–Si–C(6), 102.6 (2); C(4)–Si–C(7), 119.9 (2); C(5)–Si–C(6), 103.2 (2); C(5)–Si–C(7), 110.4 (2); C(6)–Si–C(7), 112.3 (2); C(2)–Mn–C(3), 87.3 (2); C(2)–Mn–C(4), 88.2 (2); C(3)–Mn–C(4), 88.8 (2); Mn–P(1)–C(5), 108.5 (1), Mn–P(1)–C(16), 122.2 (1); Mn–P(1)–C(26), 113.3 (1); C(5)–P(1)–C(16), 106.6 (2); Mn–C(1)–O(1), 175.0 (4); Mn–C(2)–O(2), 175.3 (5); Mn–C(3)–O(3), 177.2 (4); Mn–C(4)–Si, 105.1 (2); P(1)–C(5)–Si, 105.7 (2); P(2)–C(6)–Si, 105.2 (1).

of an intramolecular metalation of a CH_3–Si moiety on an organophosphorus ligand attached to manganese. This appears to be the first reported instance of C–H activation by manganese under classical reaction conditions.

Although the published coordination chemistry of chelating ditertiary phosphines is extensive,[4] only recently has there been a significant focus on organosilicon-substituted diphosphines in which silicon is either appended to[5] or substituted for[6] a carbon atom in the alkane chain linking the donor sites of the chelating ligand. We have been examining the coordination chemistry of $(C_6H_5)_2PCH_2Si(CH_3)_2CH_2P(C_6H_5)_2$ (L-L) as a continuation of earlier studies of steric effects[7] and conformational analysis of chelating phosphorus donor ligands.[8]

In general, (L-L) behaves as a typical chelating diphosphine and forms well-defined octahedral complexes such as $W(CO)_4$(L-L), *fac*-$BrMn(CO)_3$(L-L), and *fac*-$CH_3C(O)Mn(CO)_3$(L-L).[9] However, contrary to expectation,[7,8] *fac*-$CH_3Mn(CO)_3$(L-L) (1) was not isolable from the direct reaction between $CH_3Mn(CO)_5$ and (L-L) in refluxing toluene. Instead, the unique, pale yellow, air-stable, crystalline complex 2 was isolated.[10] Although 2 was identified as a facial manganese tricarbonyl derivative from the IR-active metallocarbonyl stretching bands at 1995 (s,sh), 1925 (m), and 1878 (m) cm^{-1}, the ^1H NMR spectrum of 2 was indicative of significant structural modification, the extent of which was realized only after the molecular structure had been determined.[11]

Scheme I



$$CH_3Mn(CO)_5 + (C_6H_5)_2P\text{-}CH_2\text{-}Si(CH_3)_2\text{-}CH_2\text{-}P(C_6H_5)_2 \xrightarrow[-CH_4]{-2CO}$$

2

The facial geometry of complex 2, as revealed by the molecular structure shown in Figure 1, is dictated by the unique C,P,P-tridentate ligand. The architecture of the complex is reminiscent of a substituted norbornane with manganese and silicon atoms at the bridgehead positions. The significant structural parameters of 2 are listed beneath Figure 1. None of the bond lengths is unusual as all values agree well with reported values for numerous other organometallic compounds containing either chelating phosphorus donor or (trimethylsilyl)methyl ligands. As expected, the listed bond angles at the sites of attachment of the organophosphorus ligand to manganese are close to values expected for octahedral coordination; the P–Mn–P angle is 92.6° and an average value of 83.2° is found for the two P–Mn–CH_2 intrachelate angles. These acute bonding angles centered at manganese appear to influence the structure of the ligand as the intra-ring bond angles centered at silicon average 103°. The other skeletal bond angles of the bicyclic system are near normal for tetrahedral coordination and fall in the 105–110° range.

Compound 2 has a symmetrical structure in solution ($CDCl_3$) as revealed by its remarkably simple, ambient-temperature 200-MHz ^1H NMR spectrum in the aliphatic region. The spectrum consists of three signals [assignment, chemical shift vs TMS, δ 0 (relative intensity), signal profile (coupling parameters)]: Mn–CH_2, –0.526 (2), apparent triplet ($^3J_{HP}$, $^3J_{HP'}$ = 8.7 Hz); Si–CH_3, 0.651 (3), singlet; P–CH_2, 1.483 (4), filled apparent triplet ($^2J_{HP} + {}^4J_{HP'}$ = 8.6 Hz). A somewhat unusual feature is the minimum chemical shift differentiation between the endo and exo protons of the P–CH_2 moieties. Normally, these protons

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(10) Synthesis of 2. A mixture of bis((diphenylphosphino)methyl)dimethylsilane (1.5 mmol) and methylmanganese pentacarbonyl (1.0 mmol) in dry toluene (15 mL) was heated at reflux under nitrogen for 12 h. The light brown reaction mixture was filtered through silica gel under nitrogen to yield a clear yellow-green solution. Dry hexane (15 mL) was added to the solution and upon standing overnight yielded 2, mp 203–206 °C dec. Anal. Calcd for $C_{31}H_{29}MnO_3P_2Si$: C, 62.63; H, 4.92. Found: C, 62.40; H, 4.85.

(11) Crystal data for $C_{31}H_{29}O_3P_2SiMn$ (2): monoclinic, $P2_1/c$, a = 10.038 (2) Å, b = 17.726 (3) Å, c = 16.216 (4) Å, β = 99.46 (2)°, V = 2877 (1) Å^3, Z = 4, D(calcd) = 1.37 g cm^{-3}, μ(Mo Kα) = 6.20 cm^{-1}. No correction for absorption was required (regular crystal shape, low μ). Of 4174 data collected (23 °C, Nicolet R3m diffractometer, $4° \le 2\theta \le 46°$), 4008 were independent and 2686 were observed ($5\sigma(F_o)$). Direct methods located the Mn, Si, and P atoms. All non-hydrogen atoms were anisotropically refined and all hydrogen atoms were treated as idealized, isotropic contributions. The phenyl rings were constrained to rigid hexagons to conserve data. $R(F)$ = 4.23%, $R(wF)$ = 4.46%, GOF = 1.089, and $\Delta(\rho)$ = 0.28 e Å^{-3}. All computations used the SHELXTL (5.1) program library (G. W. Sheldrick, distributed by Nicolet XRD, Madison, WI).

should exhibit AB coupling and both two-bond and four-bond coupling to the magnetically nonequivalent phosphorus nuclei.

In a formal sense, as suggested in Scheme I, 2 may be regarded as the product of a reaction between (L-L) and $CH_3Mn(CO)_5$ in which one molecule of methane and two molecules of carbon monoxide are eliminated per mole of reagents. Alternatively, the eliminated species might be acetaldehyde and carbon monoxide or even ketene and dihydrogen. At this time, no substance other than 2 has been identified as a product of this reaction. Although the initial steps in the overall process leading to 2 probably include well understood reactions such as methyl migration and decarbonylation, no unique mechanism for subsequent steps (e.g. agostic and/or four-center interactions)[12] can be advanced at this time. Nevertheless, the overall process most likely involves (1) loss of a methyl or acetyl group attached to manganese and (2) metalation of a methyl group on silicon. Precedence has been established for each of these two processes, as shown in the following paragraphs. However, to our knowledge, there has been no previously reported observation of these two processes occurring simultaneously, or in a stepwise manner, at manganese.

Two reports of reductive elimination of an alkane in which the alkyl moiety resides originally on manganese may be cited. Kaesz and his co-workers observed elimination of methane in the reactions between $CH_3Mn(CO)_5$ and bis(cyclopentadienyl)tungsten, -molybdenum, and rhenium hydrides.[13] Later, Halpern and his co-workers showed a similar elimination of substituted toluenes or phenylacetaldehydes from selected benzylmanganese carbonyl complexes upon reaction with related hydridomanganese carbonyl complexes.[14] The latter study showed very clearly that at least four different modes of reductive elimination are possible in this chemistry.

The activation of C–H bonds in tetramethylsilane by alkylmetal complexes was first reported by Watson.[15] Specifically, $(\eta^5\text{-}C_5Me_5)_2Lu\text{–}CH_3$ was observed to react with tetramethylsilane at 40 °C in cyclohexane with elimination of methane and formation of the metalated product $(\eta^5\text{-}C_5Me_5)_2Lu\text{–}CH_2SiMe_3$. Similar activation of tetramethylsilane by thorium derivatives was demonstrated by Marks and his co-workers.[16]

The formation of 2 under our reaction conditions appears to be an example of a facile intramolecular process that incorporates the two well-documented types of intermolecular reactions described above. The ease with which this intramolecular reaction occurs at manganese is reasonable inasmuch as C–H bond activation has been demonstrated to occur readily whenever intramolecular reaction is possible.[17]

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Registry No. 2, 114762-77-5; $(C_6H_5)_2PCH_2Si(CH_3)_2SiCH_2P(C_6H_5)_2$, 59557-18-5; $CH_3Mn(CO)_5$, 13601-24-6.

Supplementary Material Available: ORTEP drawing and a 3D stereoplot and tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom and atomic coordinates (7 pages); listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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A Convenient Route to an Uncommon Class of Polymeric and Binuclear Ruthenium(I) Complexes Containing Diphosphine and Dithioether Ligands

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Summary: Reaction of either the carboxylate-bridged dimers $[Ru(CO)_2(\mu\text{-}O_2CR)(NCMe)]_2$ or the polymeric dimers $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2]_n$ (R = Me, Et) with 1 equiv (per dimer unit) of the bidentate groups L_2 ($L_2 = R'_2PCH_2PR'_2$, R′ = Ph (DPPM), Me (DMPM); $L_2 = R'SCH_2SR'$, R′ = Ph, Me) yields the unusual Ru(I) polymers $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(L_2)]_n$, in which two metals are bridged by two carboxylate groups and these binuclear units are linked by diphosphine or dithioether ligands. Reaction with 2 equiv of the diphosphine $Ph_2PCH_2PPh_2$ in THF yields the neutral disubstituted dimer $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2(\eta^1\text{-}DPPM)_2]$, whereas with DPPM or $Ph_2P(CH_2)_2PPh_2$ (DPPE) in alcohols two types of cationic compounds of formula $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(L_2)_2]^+$ (L_2 = DPPM, DPPE) are obtained. The X-ray structures of both cationic species have been determined and show that one has the Ru(I) centers bridged by two DPPM and one acetate ligand, whereas the other has two bridging carbonyls and one bridging acetate group, with one DPPE chelating each metal.

The recent interest in binuclear complexes, particularly of the group 8 metals, has been brought about, to a large degree by the anticipation that such complexes may display metal–metal cooperativity effects in substrate activation and catalysis.[1-5] One major class of binuclear

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