increases to 4400 Hz (δ −13) at 0.146 M. From these values, we calculated that the amount of free ion varies for Me_3GeClO_4 from 99% at 0.001 53 M to 6.4% at 0.584 and for Ph_3GeClO_4 from 99% at 0.001 555 M to 4.4% at 0.146 M. By comparison, the line width of $HClO_4$ in sulfolane is 10–25 Hz in the concentration range 0.00225–0.146 M.

Charge distribution within the phenyl ring was explored by comparison of the ^{13}C chemical shifts of Ph_3GeH and Ph_3Ge^+. The ipso and ortho shifts are not useful because of the normal α and β effects. The meta resonance moves from δ 128.33 to δ 128.27 on cation formation in CH_2Cl_2 and the para resonance from δ 129.14 to δ 131.9. Such shifts are consistent with the modest charge buildup expected of ion pairs at high concentrations.

These results are interpretable only in terms of monomeric, ionic germylenium ions in dilute sulfolane solution: high conductance, two-particle molecular weight, and sharp ^{35}Cl line width. Association occurs at higher concentrations in sulfolane and in less polar solvents such as dichloromethane.

Registry No. Me_3Ge^+, 76568-90-6; Ph_3Ge^+, 41099-51-8.

Unprecedented Transformation of a Vinylidene Ligand. Synthesis and ESR Characterization of a Paramagnetic σ-Acetylide Complex of Rhodium(II)

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Summary: Thermal decomposition in THF of the diamagnetic vinylidene complex $[(np_3)RhC{=}C(H)Ph]^+$, obtained by protonation of $[(np_3)RhC{\equiv}CPh]$, affords H_2 and the paramagnetic σ-acetylide complex of rhodium(II) $[(np_3)RhC{\equiv}CPh]^+$ which has been characterized by chemical, electrochemical, and ESR techniques [$np_3 = N(CH_2CH_2PPh_2)_3$].

The key role of the vinylidene group in many catalytic processes involving carbon monoxide or unsaturated hydrocarbons is certainly one of the reasons for experimental[1] and theoretical[2] studies presently carried out on vinylidene complexes of transition metals. In this communication we report on an unprecedented transformation of the vinylidene ligand in $[(np_3)RhC{=}C(H)Ph]BPh_4$[3] (1) [$np_3 = N(CH_2CH_2PPh_2)_3$].

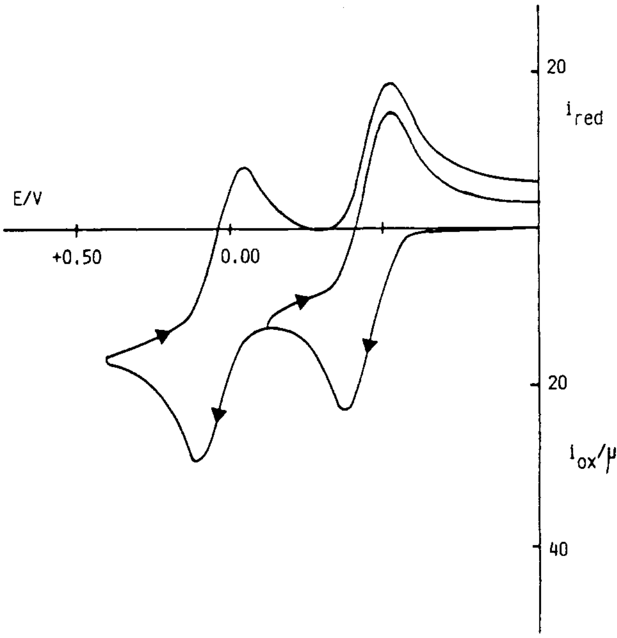
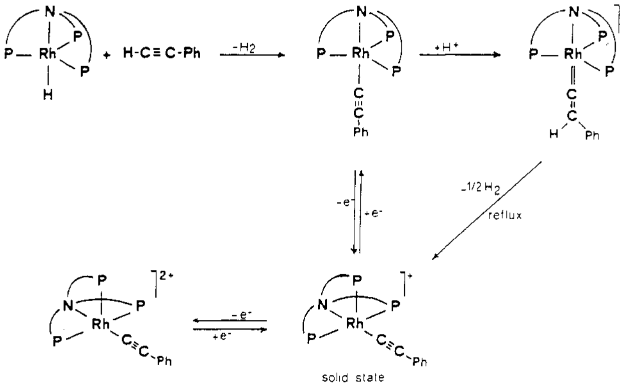


Figure 1. Cyclic voltammogram recorded at a platinum electrode on a THF solution containing $[(np_3)RhC{\equiv}CPh]$ (1.70×10^{-3} mol dm^{-3}) and $[NBu_4]ClO_4$ (0.1 mol dm^{-3}) (scan rate 0.2 V s^{-1}).

Scheme I



Compound 1 is synthesized as deep red crystals by protonation of $[(np_3)RhC{\equiv}CPh]$[4] (2) in THF by $HOSO_2CF_3$, followed by addition of $NaBPh_4$ in ethanol (yield 70%) (Scheme I). The neutral σ-acetylide 2 is prepared quantitatively by treatment of $[(np_3)RhH]$[5] (3) in THF with a twofold excess of $HC{\equiv}CPh$.[6] The vinylidene complex 1 is trigonal-bipyramidal (TBP) as deduced by analysis of the ^{31}P and ^1H NMR spectra. In particular, the $^{31}P\{^1H\}$ NMR spectrum exhibits an A_3X spin system

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(1) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Hilton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

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(3) Anal. Calcd (Found): C, 75.07 (75.45); H, 5.93 (5.82); N, 1.10 (1.19); Rh, 8.52 (8.74). IR (Nujol): $\nu(C{=}C)$ 1640 (m), phenyl-reinforced vibration 1590 cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz, TMS, 298 K): δ 4.93 [qd, 1 H, $^4J(HP)$ = 13.8 Hz, $^3J(HRh)$ = 1.1 Hz, $=CH$]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 32.19 MHz, H_3PO_4 85%, 298 K): A_3X pattern, $\delta(P_A)$ 37.86 [$J(PRh)$ = 136.8 Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.43 MHz, TMS, 298 K): δ 316.82 [dq, $J(CRh)$ = 44.2 Hz, $^2J(CP)$ = 20.0 Hz, C_α of the vinylidene ligand]; the β-carbon resonance was not conclusively identified as it lies under the phenyl multiplets. Like many vinylidene complexes, 1 is deprotonated by a base such as NEt_3 to form the starting σ-acetylide and $[NEt_3H]^+$.

(4) Anal. Calcd (Found): C, 69.79 (70.01); H, 5.63 (5.52); N, 1.59 (1.63); Rh, 11.87 (12.00). IR (Nujol): $\nu(C{\equiv}C)$ 2080 (s), phenyl-reinforced vibration 1590 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): A_3X pattern, $\delta(P_A)$ 24.68 [$J(PRh)$ = 160.7 Hz].

(5) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1987**, 971.

(6) In the course of the reaction H_2 is evolved as determined by GC.

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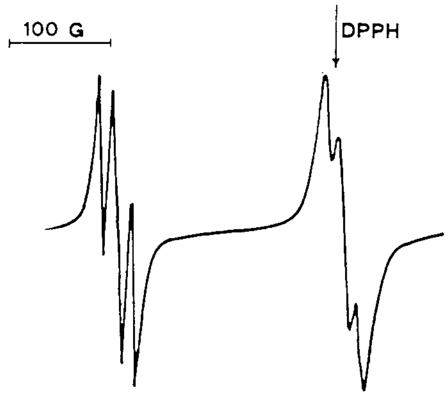

Figure 2. X-band ESR spectrum of $[(np_3)RhC{\equiv}CPh]BPh_4$ in THF at 298 K.

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 [ν(C$\equiv$C) = 2115 cm^{-1}], is paramagnetic with a magnetic moment corresponding to one unpaired spin (μ_{eff} = 1.90 μ_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{^{1}H} NMR data, **5** is assigned a SQ structure (AM$_2$X 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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[7] Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Sabat, M.; Zanobini, F. *Organometallics* **1986**, *5*, 2557. Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Sabat, M. *Ibid.* **1985**, *4*, 1014.

[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): ν(C$\equiv$C) 2115 (w), phenyl-reinforced vibration 1590 cm^{-1}.

[9] Bencini, A.; Gatteschi, D. *Transition Met. Chem.* (*N.Y.*) 1982, *8*, 1.

[10] Zotti, G.; Zecchin, S.; Pilloni, G. *J. Electroanal. Chem.* **1984**, *175*, 241.

[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]

[12] Wilson, R.; Kivelson, D. J. *J. Chem. Phys.* **1966**, *44*, 4445.

[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): ν(C$\equiv$C) 2125 (m), phenyl-reinforced vibration 1600 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 213 K): AM$_2$X pattern, δ(P$_A$) 33.71 [J(P$_A$P$_M$) = 22.6 Hz, J(P$_A$Rh) = 129.3 Hz], δ(P$_M$) 23.43 [J(P$_M$Rh) = 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 ^{1}H 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$_3$Mn(CO)$_5$ and (C$_6$H$_5$)$_2$PCH$_2$Si(CH$_3$)$_2$CH$_2$P(C$_6$H$_5$)$_2$. The crystal and molecular structure of the product of the reaction, (OC)$_3$Mn–CH$_2$Si(CH$_3$)(CH$_2$P(C$_6$H$_5$)$_2$)$_2$, 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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[1] (a) West Chester University. (b) Lehigh University (c) University of Delaware.

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