electrons. Each $V(CO)_2(C_5H_5)$ unit also carries a poorly hybridized V 3d orbital which is partly delocalized onto the CO ligands, is fully occupied, and plays little role in the bonding of the $V_2P$ moiety. Linear combinations of the remaining $\sigma$ and $\pi$ orbitals on the $V(CO)_2(\eta\text{-}C_5H_5)$ and $\mu$-PR fragments give rise to an orbital pattern reminiscent of a heterocyclopropenium ion (Figure 2). Thus there are three occupied in-plane orbitals that form the $\sigma$-framework of the ring and one occupied symmetric out-of-plane $\pi$ orbital. This description implies a formal V–V bond order slightly greater than unity although V–V bonding is strongly mediated by the bridging phosphinidene. In terms of the isolobal analogy[20] $V(CO)_2(\eta\text{-}C_5H_5)$ is behaving like $CH^+$ and PH as $CH^-$, giving the observed analogy between 1 and $C_3H_3^+$.

Further examples of group 5 phosphinidenes are being sought, and the reactivity of 1 is under investigation.

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**Registry No.** 1, 105472-74-0; $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)PCl_2$, 79074-00-3; $Na_2[\eta^5\text{-}C_5H_5)V(CO)_3]$, 68688-11-9; V, 7440-62-2.

**Supplementary Material Available:** Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for 1 (11 pages); a listing of observed and calculated structure factors (15 pages). Ordering information is given in any current masthead page.

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(20) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148. Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

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# A Convenient and Novel Route to Bis(η-alkyne)platinum(0) and Other Platinum(0) Complexes from Speier's Hydrosilylation Catalyst $H_2[PtCl_6]\cdot xH_2O$. X-ray Structure of $[Pt\{(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}(P\text{-}t\text{-}Bu_3)]$

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*Summary:* Evidence that the hydrosilylation catalyst, obtained by refluxing $H_2[PtCl_6]\cdot xH_2O$ in $(Me_2ViSi)_2O$ (solution A), is a Pt(0) species comprises (i) the isolation and X-ray characterization of $[Pt\{(\eta\text{-}CH_2CHMe_2Si)_2O\}(P\text{-}t\text{-}Bu_3)]$, after addition of $P\text{-}t\text{-}Bu_3$ to A, (ii) the convenient high-yield synthesis of various other Pt(0) complexes from A, and (iii) CV, GC/MS, and $^{195}Pt$ NMR data.

Despite the widespread application of Speier's catalyst, chloroplatinic acid, there is still uncertainty about the nature of the initiator in the catalytic hydrosilylation cycle.[1,2] A useful form of $H_2[PtCl_6]\cdot xH_2O$ is obtained by treating it with a vinylsiloxane.[3] We now show that, surprisingly, such a solution (A), obtained from chloroplatinic acid and *sym*-tetramethyldivinyldisiloxane, contains Pt(0) and is a suitable starting material for a high-yield synthesis of (i) bis(η-alkyne)platinum(0) complexes or (ii) various (tertiary phosphine)platinum(0) complexes (Scheme I). We further provide definitive evidence for a chelating bis(η-vinyl) mode of bonding between $(Me_2ViSi)_2O$ and Pt(0).

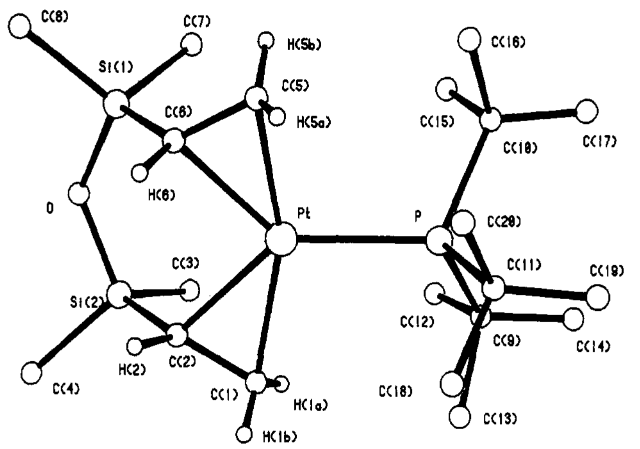
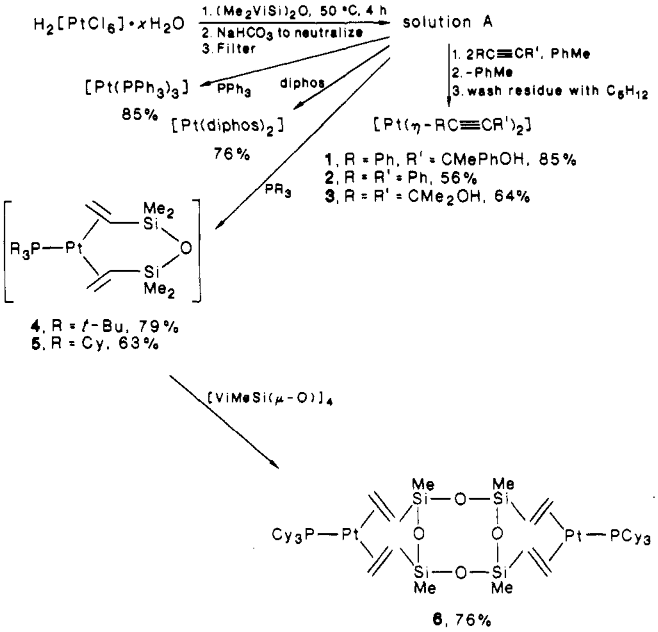


**Figure 1.** A drawing of $[Pt\{(\eta\text{-}CH_2{=}CHMe_2Si)_2O\}(P\text{-}t\text{-}Bu_3)]$ (4) showing the molecular structure and atom numbering (only the vinyl H atoms are shown). Selected bond distances (Å) and angles (deg): Pt–P = 2.384 (2), Pt–C(5) = 2.154 (12), Pt–C(6) = 2.168 (11), Pt–C(1) = 2.185 (13), Pt–C(2) = 2.172 (8); P–Pt–C(1) = 99.5 (3), P–Pt–C(2) = 137.0 (3), P–Pt–C(5) = 100.7 (3), P–Pt–C(6) = 137.9 (3), Si(1)–O–Si(2) 129.9 (4)°.

**Scheme I**



Homoleptic platinum(0) alkyne complexes were first obtained (low yield) by reduction of $K_2[PtCl_4]$ in EtOH in presence of a 1,4-dihydroxy-2-alkyne.[4] Related compounds $[Pt(\eta\text{-}RC{\equiv}CR')_2]$ were prepared (high yields) from either $[Pt(COD)_2]$ (COD = 1,5-cyclooctadiene) or $[Pt(\eta\text{-}C_2H_4)_3]$;[5] however, the latter are not readily available.[6]

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(1) For reviews, see: (a) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 330. Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(2) For a review, see: Stark, F. O.; Fallender, J. R.; Wright, A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, p 305.

(3) Willing, D. N. U.S. Patent 3 419 593, 1968. Karstedt, B. D. U.S. Patent 3 775 452, 1973.

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0276-7333/87/2306-0191$01.50/0

Our simple route to bis(alkyne)platinum(0) complexes involves treating solution A[7] with the appropriate alkyne to yield $[Pt(\eta\text{-}RC{\equiv}CR')_2]$: **1** (R = Ph, R′ = CMePhOH),[8] **2** (R = R′ = Ph),[9] and **3** (R = R′ = $CMe_2OH$)[9] (Scheme I). Attempts to prepare analogues using a terminal alkyne (e.g., $CH{\equiv}CCMe_2OH$) were unsuccessful.

Solution A is also a convenient source of other Pt(0) species. Of particular interest are the three-coordinate complexes $[Pt\{(\eta\text{-}ViMe_2Si)_2O\}(PR_3)]$ [R = *t*-Bu (**4**)[10] or Cy (**5**);[11] Vi = $CH{=}CH_2$, Cy = $C_6H_{11}$]. For one of these, **4**, X-ray data (Figure 1)[12] show that *sym*-tetramethyldivinyldisiloxane behaves as a chelating bidentate ligand. The cyclotetrakis(methylvinylsiloxane) is believed to function as a tetradentate chelating and bridging ligand in $[\{Pt(PCy_3)\}_2\{ViMeSi(\mu\text{-}O)\}_4]$ (**6**);[13-15] there was no evidence for different types of coordinated vinyl groups in **6**.

The data of Scheme I indicate that solution A contains Pt(0). Additional confirmation is provided by cyclic voltammetry (CV)[16] and NMR data (vide infra).

A well-defined quasi-reversible redox couple was observed in the oxidative CV scan of solution A, while no reduction occurred out to a potential of −2 V.[16] Evidently, the Pt(IV) in chloroplatinic acid is completely reduced to Pt(0) during its reaction with $(Me_2ViSi)_2O$ to yield A.

GC/MS examination of the Pt-free volatile materials from solution A showed them to have the composition $Me_2RSiO(SiMe_2O)_xSiRMe_2$ ($x$ = 0–14, but mainly $x$ = 0; R = mainly Vi, some Et, and a trace of $CH_2CH_2Cl$). $^{195}Pt$ NMR of solution A (77 MHz, in $C_6D_6$ relative to $K_2[PtCl_4]$) showed a signal at −4534 ppm; this is close to that found (−4520 ppm) for the product obtained from $[Pt(COD)_2]$ + $4(Me_2ViSi)_2O$.[17]

From all the above data, we suggest that solution A contains preponderantly $[Pt\{\eta\text{-}Me_2ViSiO(Me_2SiO)_xSiMe_2Vi\text{-}\eta\}_y]$ ($x$ = 0–14, but mainly $x$ = 0; and $y$ = 2–4, but mainly $y$ = 2).

The Pt, P, and vinyl C atoms in **4** are coplanar to within 0.1 Å. The H and Si atoms attached to the vinyl groups are slightly bent away from the Pt atom. The dimensions Pt—P = 2.384 (2) Å, C═C = 1.40 (2) Å, and average Pt–C = 2.170(12) Å are unexceptional, cf. data for $[Pt(\eta^2\text{-}C_6Me_4O_2)(\eta\text{-}C_2H_4)(PCy_3)]$[18] and $[Pt(\eta\text{-}C_2H_4)(\eta\text{-}C_2F_4)(PCy_3)]$,[19] for both of which the $C_2H_4$ group is in the coordination plane of Pt. Thus, in 4 the Si–O–Si chain bridging the two vinyl groups has only a minor effect on the coordination geometry.

In summary, the chemistry presented in Scheme I is unusual and has significant implications. First, it indicates that the initiator in the $H_2[PtCl_6]\cdot xH_2O$–vinylsiloxane hydrosilylation system is a bis($\eta$-vinyl)-chelating Pt(0) complex; specifically, solution A probably has $\overline{Pt}\text{-}\overline{(CH_2}{=}\underline{CHMe_2SiOSiMe_2CH{=}CH_2)_2}]$ as the principal ingredient. Secondly, solution A is a convenient source of well-defined Pt(0) complexes; it may be a simple alternative to "naked" platinum complexes such as the synthetically versatile $[Pt(\eta\text{-}C_2H_4)_3]$ or $[Pt(COD)_2]$.[20] Thirdly, vinylsiloxanes such as $(Me_2ViSi)_2O$ are unexpectedly effective as reducing agents, both of Pt(IV) and Pt(II) (the mechanism of the reductions is being investigated). Fourthly, we predict that $(Me_2ViSi)_2O$, or analogues, may similarly afford derivatives of other noble metals in low oxidation states, e.g., siloxane–Rh(I) solutions from $RhCl_3\cdot 3H_2O$. Finally, the chelating ($\eta$-divinyldisiloxane)platinum(0) complexes **4**–**6** have structural novelty and a potentially rich chemistry.

**Acknowledgment.** We thank Drs. A. G. Avent and M. C. Misra for the NMR data and Dr. R. M. Van Effen for the cyclic voltammetry experiment.

**Supplementary Material Available:** Tables of analytical and crystal data, bond lengths and angles, fractional atomic coordinates, and anisotropic temperature factors for compound 4 (6 pages); a listing of structure factor for compound 4 (14 pages). Ordering information is given on any masthead page.

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(6) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271. Spencer, J. L. *Inorg. Synth.* **1979**, *19*, 213.

(7) In a typical experiment, $H_2[PtCl_6]\cdot xH_2O$ (5.0 g) in water (0.6 g) was heated under reflux with $(Me_2ViSi)_2O$ (50 g) at 50 °C for 4 h; the volatiles ($C_2H_4$, $C_4H_6$, and HCl) were not trapped. The cooled reaction mixture was neutralized with $NaHCO_3$ (5.0 g, added in small portions) and filtered. The yellow chloride-free filtrate of solution A contained 4.06% Pt (atomic absorption). [$NaHCO_3$ has no reducing role, since solution A was also obtained when the neutralization step was omitted.]

(8) Compound 1 was obtained by adding solution A[7] [5.4 g (1.1 mmol of Pt)] to a toluene solution (14 mL) containing 0.52 g (2.3 mmol) of $PhC{\equiv}CR$ (R = CMePhOH); after 5 h at ca. 20 °C, the PhMe was removed under vacuum and the residual solid 1 (0.62 g), mp 99–101 °C, was washed with $C_5H_{12}$ (3 × 5 mL) and dried under vacuum. Its identity was confirmed by its IR ($\nu_{C\equiv C}$ 1889 $cm^{-1}$) and NMR spectra and satisfactory C and H analyses.

(9) Compounds **2** and **3** were prepared and characterized in a similar fashion to that described for 1.[8]

(10) White crystals [from solution A,[7] containing 8.2 mmol of Pt and $P\text{-}t\text{-}Bu_3$ (1.80 g, 8.9 mmol): heating for 5 min at 65 °C, cooling to ca. 20 °C, filtering, washing with $(Me_2ViSi)_2O$, and drying under vacuum], mp 145–147 °C dec; satisfactory C, H, P, Pt, and Si analyses; $^{195}Pt$ NMR ($C_6D_6$, 77 MHz, relative to $K_2[PtCl_4]$) −4103.7 ppm (d, $J_{PtP}$ = 3732.9 Hz).

(11) White solid [obtained as for 4,[10] from solution A, containing 16.4 mmol of Pt and $PCy_3$ (5.0 g, 17.9 mmol) at 85 °C for 5 min], mp 188–189 °C dec; satisfactory C, H, P, and Si analyses.

(12) Crystal data: $C_{20}H_{45}OPPtSi_2$; $M_r$ 583.8; triclinic, space group $P\bar{1}$; $a$ = 9.447 (3) Å, $b$ = 11.453 (3) Å, $c$ = 12.788 (4) Å, $\alpha$ = 71.77 (2)°, $\beta$ = 79.18 (3)°, $\gamma$ = 78.34 (2)°; $Z$ = 2; $\mu$(Mo K$\alpha$) = 57.2 $cm^{-1}$. The structure was solved by Patterson and Fourier techniques and refined to a conventional $R = 0.038$ ($R_w = 0.048$) by using 2805 reflections with $I > \sigma(I)$, measured on an Enraf-Nonius CAD-4 diffractometer, in least-squares refinement (Pt, P, Si, O, and C anisotropic). Vinyl H atoms were refined while *tert*-butyl H atoms were fixed at calculated positions. An empirical absorption correction was applied on the basis of psi scan measurements.

(13) White crystals [by heating **5** (0.50 g, 0.76 mmol) and $\{MeViSi(\mu\text{-}O)\}_4$ (a mixture of isomers) (0.5 g, 1.42 mmol) at 100 °C for 2 min, cooling to ca. 20 °C, filtering, washing with $C_5H_{12}$, and drying under vacuum], mp > 300 °C; satisfactory C, H, and Si analyses.

(14) Cf. $SiVi_4$ reacts with $[Fe(CO)_5]$ to yield $[\overline{Fe(CO)_3\{(CH_2{=}}CH)_2\text{-}Si(CH{=}\overline{CH_2)_2\}}Fe(CO)_3]$.[15]

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(16) In the CV system (Van Effen, R. M.; Evans, D. H. *J. Electroanal. Chem.* **1979**, *103*, 383), the working electrode was glassy carbon, and a saturated calomel electrode (SCE) was the standard; the electrolyte solvent was 0.2 M $[N\text{-}n\text{-}Bu_4][ClO_4]$ in $CH_2Cl_2$; the working electrode potential was scanned at 500 mV $s^{-1}$ with initial, reversal, and final potentials raised as necessary; the scan rate was 0.5 V $s^{-1}$.

(17) This solution was obtained from $[Pt(COD)_2]$ (0.40 g, 0.97 mmol) and $(Me_2ViSi)_2O$ (0.72 g, 3.88 mmol) in PhMe (15 mL) at ca. 20 °C; after ca. 4 h volatiles were removed in a vacuum to leave an oil (0.50 g), the $^1H$ NMR of which showed Me and Vi, but no COD, signals.

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(20) For a review, see: Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318.