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Vanadium-phosphinidene complex exhibiting vanadium-phosphorus multiple bonding

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methods give a bond length ordering of $Ge{=}O < Ge{=}N < Ge{=}C$, with a concomitant decrease in the stretching vibrational frequencies. The MNDO frequencies are in better agreement with the ab initio SCF values than with the CI results.

For digermene (Ge_2H_4) the situation is different. While MNDO gives a planar structure, ab initio MO calculations yield a nonplanar, trans-folded structure with the angle θ between the Ge–Ge bond and the GeC_2 plane being 40°. This latter result agrees with the X-ray structure of Ge_2R_4, $[R{=}CH(Si(Me_3)_2]$[24] which has a fold angle of 32°. The analogous Sn structure has a fold angle of 41°,[24] indicating an even weaker M–M bond.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. AFOSR 86-0022), the Robert A. Welch Foundation (Grant No. F-126), and the National Science Foundation (Contract CHE82-17948). The calculations were carried out by using a Digital VAX 11/780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. GeF, 14929-46-5; GeCl, 21110-21-4; GeBr, 25884-11-1; GeF_2, 13940-63-1; $GeCl_2$, 10060-11-4; $GeBr_2$, 24415-00-7; GeI_2, 13573-08-5; GeH_4, 7782-65-2; $GeCl_4$, 10038-98-9; $GeBr_4$, 13450-92-5; GeI_4, 13450-95-8; $GeCl(CH_3)_3$, 1529-47-1; $GeBr(CH_3)_3$, 1066-37-1; $Ge(CH_3)_4$, 865-52-1; $Ge(CH_3)_3(t\text{-Bu})$, 1184-91-4; $Ge(CH_3)_3NMe_2$, 13361-67-6; $Ge(CH_3)_3OC_2H_5$, 4848-66-2; $Ge(C_2H_5)_4$, 597-63-7; $Ge(OCH_3)_4$, 992-91-6; $[Ge(CH_3)_3]_2O$, 2237-93-6; $Ge_2(CH_3)_6$, 993-52-2; Ge_2H_6, 13818-89-8; Ge_3H_8, 14691-44-2; $Ge(CH_3)_3^+$, 76568-90-6; $Ge(CH_3)_3$, 21941-60-6; $GeSn(CH_3)_6$, 16393-89-8; $Ge(CH_3)_2F_2$, 811-70-1; GeH_2, 24968-55-6; H_2GeGeH_2, 82323-93-1; H_2GeCH_2, 60188-36-5; H_2GeNH, 83025-94-9; H_2GeO, 78812-54-1; $Ge(CH_3)_2H_2$, 1449-64-5; $Ge(CH_3)_2Cl_2$, 1529-48-2; Ge, 7440-56-4.

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[24] Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480.

[25] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Communications

A Vanadium–Phosphinidene Complex Exhibiting Vanadium–Phosphorus Multiple Bonding

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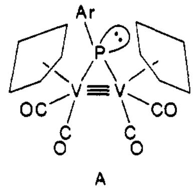
Summary: The reaction of $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)PCl_2$ with $Na_2[(\eta\text{-}C_5H_5)V(CO)_3]$ affords the bridging phosphinidene complex $[V_2(CO)_4(\eta\text{-}C_5H_5)_2\{\mu\text{-}P(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}]$ (1). The nature of the bonding in 1 is discussed on the basis of spectroscopic and X-ray crystallographic data and preliminary EHMO calculations. Compound 1 crystallizes in the triclinic space group $P\bar{1}$ with a = 9.954 (2) Å, b = 11.562 (2) Å, c = 14.362 (3) Å, α = 109.82 (2)°, β = 94.09 (2)°, and γ = 100.85 (2)°.

Phosphinidene (phosphanediyl) complexes of the type $RP(ML_n)_2$ are attracting significant recent attention. The known complexes feature either 16- or 15-electron fragments with transition metals from groups 6–8.[1] We report (i) the first group 5 phosphinidene complex and (ii) the first example of a phosphinidene moiety bonded to a *14*-electron organometallic fragment.

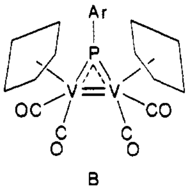
Equimolar quantities of $ArPCl_2$ (Ar = 2,4,6-t-$Bu_3C_6H_2$) and $Na_2[(\eta\text{-}C_5H_5)V(CO)_3]$[2] were allowed to react in THF solution at 25 °C. After removal of the THF, the resulting dark brown residue was extracted with n-hexane and purified by column chromatography (Florisil/n-hexane). This afforded $[(\eta\text{-}C_5H_5V(CO)_4]$ and a dark green solution from which crystals were obtained at −20 °C, corresponding to the composition $[V_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}PAr)$ (1), 28% yield.

The diamagnetism of 1 was established by the observability of (noncontact shifted) ^1H and ^{13}C NMR spectra which exhibited peaks corresponding to C_5H_5 and 2,4,6-t-$Bu_3C_6H_2$ groups.[3] No metal hydride resonances were detected within the range +10 to −20 ppm. The 121.5-MHz $^{31}P\{^1H\}$ spectrum comprised a broad singlet at δ +670 which is in the region characteristic of μ-phosphinidine complexes,[1,4] while the IR spectrum of 1 was indicative of the presence of four CO ligands.[3]

If each vanadium is to achieve an 18 electron configuration, two valence isomers, A and B, are possible. The



A



B

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[1] (a) For a recent review of phosphinidenes bonded to 16e organometallic fragments, see; Huttner, G. *Pure Appl. Chem.* **1986**, *58*, 585. See also; Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460. (b) For phosphinidenes bonded to 15e organometallic fragments: Arif, A. M.; Cowley, A. H.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1707.

[2] The salt $Na_2[(\eta\text{-}C_5H_5)V(CO)_3]$ was prepared from $(\eta\text{-}C_5H_5)V(CO)_4$ and sodium amalgam in THF following the procedure of Fischer and Schneider (Fischer, E. O.; Schneider, R. J. J. *Chem. Ber.* **1970**, *103*, 3684).

[3] NMR data for 1 in C_6D_6 (25 °C): ^1H 8.08 (d, 2H,C_6H_2, $^4J_{PH}$ = 2.5Hz), 5.36 (s, 5H, C_5H_5), 1.62 (s, 9H p-$C(CH_3)_3$), 1.48 (s, 18H, o-$C(CH_3)_3$). $^{13}C\{^1H\}$ 124.3 (d,m-C_6H_2, $^3J_{PC}$ = 8Hz), 99.5 (s, C_5H_5), 34.1 (s, p-$C(CH_3)_3$), 32.1 (s, o-$C(CH_3)_3$). The carbonyl carbons were not detected, presumably because coupling to ^{51}V and long relaxation times. IR: $\nu_{C=O}$ (n-hexane) 1985(m), 1930(s), 1855(m)cm^{-1}.

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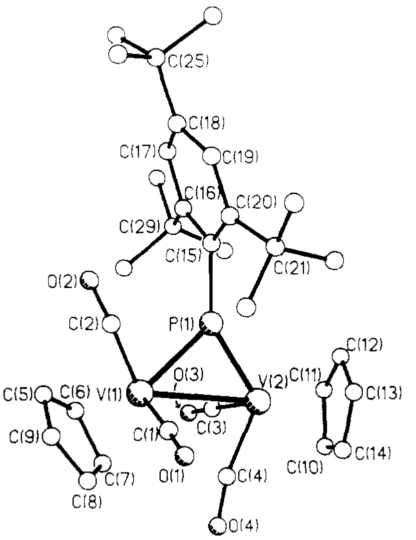

Figure 1. View of $[V_2(CO)_4(\eta\text{-}C_5H_5)_2\{\mu\text{-}P(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}]$ (1). Important parameters: P(1)–V(1) = 2.268 (1), P(1)–V(2) = 2.243 (1), V(1)–V(2) = 2.924 (1), P(1)–C(15) = 1.840 (3) Å; V(1)–P(1)–V(2) 80.83 (3); V(1)–C(1)–O(1) = 177.4 (3), V(1)–C(2)–O(2) = 175.8 (3), V(2)–C(3)–O(3) = 177.2 (4), V(2)–C(4)–O(4) = 168.0 (3), V(1)–P(1)–C(15) = 130.2 (1), V(2)–P(1)–C(15) = 149.0 (1)°.

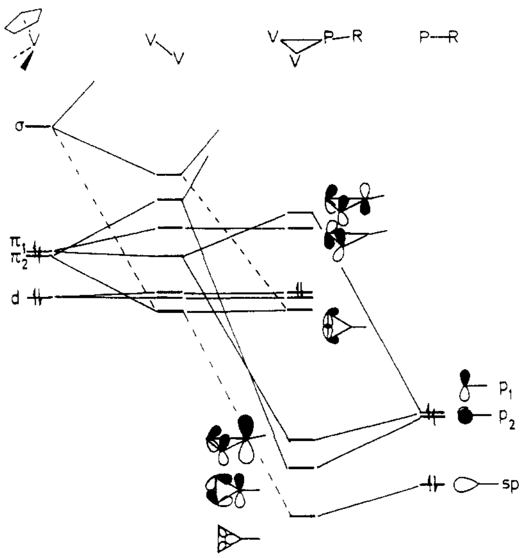

Figure 2. Qualitative orbital correlation diagram for the construction of the V_2P ring orbitals in 1 from $V(CO)_2(\eta\text{-}C_5H_5)$ and PR fragments. Numeric subscripts refer to out-of-plane (π_1, p_1) and in-plane (π_2, p_2) fragment orbitals.

possibility of this ambidonor bonding dichotomy for μ-phosphinidene (and heavier congeneric) complexes has been noted previously.[4,5] Thus, in order to more precisely determine the structure an X-ray diffraction study[6] was undertaken, the results of which are shown in Figure 1. The V–P distances in 1 (which average 2.255 Å) are considerably shorter than those found in, e.g., vanadium–phosphine complexes (2.47–2.49 Å).[8] Together with the trigonal-planar geometry at phosphorus, these observations imply vanadium–phosphorus multiple bonding, thus favoring structure B. The assignment of metal–metal bond order on the basis of metal–metal distances tends to be ambiguous when bridging ligands are present.[9] However, the available data suggest that a vanadium–vanadium distance of 2.200 (2) Å (in $V_2(2,6\text{-}(MeO)_2Ph)_4\cdot THF$)[10] corresponds to a triple bond, while lesser degrees of vanadium–vanadium multiple bonding have been suggested for the compounds $Cp_2V_2(CO)_5$ (2.462 (2) Å),[8b,11] $Cp_2V_2(CO)_5(PPh_3)$ (2.466 (1) Å),[8b] $(CpVH)_2C_6H_6$ (2.425 (1) Å),[12] and $[(CO)_4VPMe_2]_2$ (average 2.733 Å).[13] Clearly the vanadium–vanadium distance in 1 of 2.924 (1) Å is not indicative of substantial multiple bonding.[14] That some metal–metal interaction is present, however, is implied by the acute V(1)–P(1)–V(2) angle of 80.83 (3)°. In situations were a trigonal-planar phosphinidene group bridges a dimetal fragment with no metal–metal interaction, this angle is much larger, ~130–140°.[1,4]

Brief mention should also be made of the carbonyl ligands. Thus, while C(1)–O(1), C(2)–O(2), and C(3)–O(3) have normal terminal metal carbonyl geometries (Figure 1), C(4)–O(4) is tending toward a semibridging mode as evidenced by the angle at C(4) (V(2)–C(4)–O(4) = 168.0 (3)°). Further evidence for such an interaction is provided by the low-frequency (1855 cm^{-1}) C–O stretching vibration in the IR.[3] Nevertheless, this interaction must be described as weak since the V(1)···C(4) distance (2.793 (4) Å)[15] greatly exceeds the sum of the V and C covalent radii (1.99 Å).

We have investigated the bonding in the V_2P ring of 1 by EHMO calculations.[16] Each $V(CO)_2(\eta\text{-}C_5H_5)$[19] unit furnishes frontier orbitals of σ and π (two) pseudosymmetry, containing two electrons in total, for combination with the σ (sp hybrid) and two π (P 3p) orbitals of the phosphinidene fragment which contain a total of four

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[4] Arif, A. M.; Cowley, A. H.; Norman, N. C.; Orpen, A. G.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1267.

[5] Cowley, A. H.; Norman, N. C.; Pakulski, M.; Bricker, D, L.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 8211 and references therein.

[6] Compound 1: $C_{32}H_{39}O_4PV_2$, M_r 620.52, triclinic $P\bar{1}$; $a = 9.954$ (2) Å, $b = 11.562$ (2) Å, $c = 14.362$ (3) Å, $\alpha = 109.82$ (2)°, $\beta = 94.09$ (2)°, $\gamma = 100.85$ (2)°; $V = 1511$ (1) $Å^3$; $Z = 2$; D(calcd) = 1.364 g cm^{-3}, λ (Mo Kα) = 0.7107 Å, μ (Mo Kα) = 9.8 cm^{-1}. An empirical absorption correction was applied. The intensities of 4732 unique reflections were measured on an Enraf–Nonius CAD-4F diffractometer using the $\theta/2\theta$ scan mode at room temperature ($3.00° \le 2\theta \le 49.00°$). The structure was solved by direct methods and refined by full-matrix least squares using 2958 reflections with $I > 3.0\sigma(I)$. The final residuals were $R = 0.050$ and $R = 0.056$. All calculations were performed with the SDP-Plus program package.[7]

[7] Frenz, B. A., B. A. Frenz and Associates, Inc., College Station, TX.

[8] (a) Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 189. (b) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

[9] Cotton, F. A.; Walton, R. A. In *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

[10] Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886.

[11] Cotton, F. A.; Frenz, B. A.; Kruczynski, L. *J. Am. Chem. Soc.* **1973**, *95*, 951. Cotton, F. A.; Kruczynski, L.; Frenz, B. A. *J. Organomet. Chem.* **1978**, *160*, 93.

[12] Jonas, K.; Wiskamp, V.; Tsay, Y.-H.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5480.

[13] Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472. For a theoretical discussion of this molecule, see: Shiak, S.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 1194.

[14] The possibility of vanadium–hydrogen bonding was also considered. However, there were no peaks of residual density in the final difference map which were indicative of such atoms. The conclusion that there are no V–H bonds gains credence from the fact that all 39 hydrogens in 1 were located and refined. Moreover, no signals corresponding to hydrides were detected in ^1H NMR spectrum from δ −20 to +10. While such signals may be broad and difficult to observe because of coupling to ^{51}V, they are observed in $(CpVH_2C_6H_6)$.[12]

[15] The other V···C distances are V(1)···C(3) = 3.203 (3) Å, V(2)···C(1) = 3.485 (4) Å, and V(2)···C(2) = 4.244 (4) Å.

[16] Calculations were performed by the extended Hückel method using program ICON-8[17] on a model for 1 $[V_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}PH)]$ at a geometry derived from the crystal structure with P–H = 1.44 Å, C–H = 1.09 Å, and C_5H_5 rings with D_{5h} symmetry. Hückel parameters were taken from the literature.[18]

[17] Howell, J.; Rossi, A.; Wallace, D.; Harak, I. K.; Hoffmann, R. *QCPE* **1977**, *10*, 344.

[18] Kubacek, P.; Hoffmann, R.; Harlas, A. *Organometallics* **1982**, *1*, 180.

[19] See, e.g.: Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7812.

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 σ and π orbitals on the $V(CO)_2(\eta\text{-}C_5H_5)$ and μ-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 σ-framework of the ring and one occupied symmetric out-of-plane π 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.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support. N.C.N. thanks the Research Corp. Trust for financial support.

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.

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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Received August 12, 1986

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).

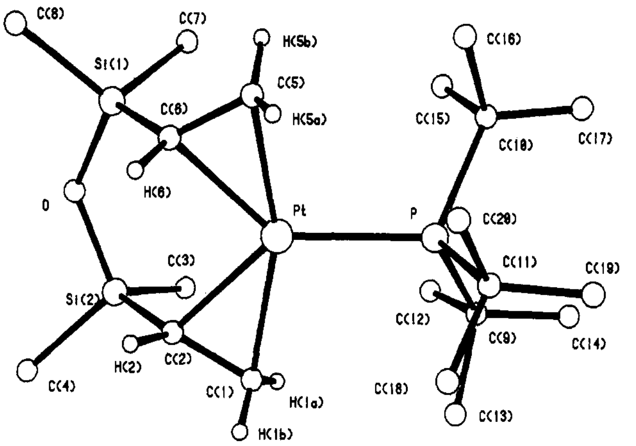
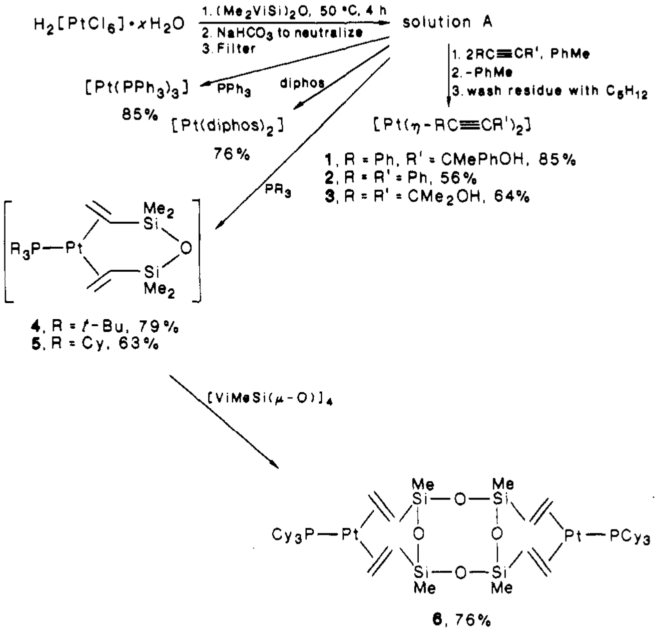


Figure 1. A drawing of $[Pt\{(\eta\text{-}CH_2{=}CHMe_2Si)_2O\}(P\text{-}t\text{-}Bu_3)]$ (4) showing the molecular structure and atom numbering (only the vinyl H atoms are shown). Selected bond distances (Å) and angles (deg): Pt–P = 2.384 (2), Pt–C(5) = 2.154 (12), Pt–C(6) = 2.168 (11), Pt–C(1) = 2.185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

[4] Rochon, F. D.; Theophanides, T. *Can. J. Chem.* **1972**, *50*, 1325.

[5] Boag, N. M.; Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2170.

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