Volume 29
Number 26
December 26, 1990

Inorganic Chemistry

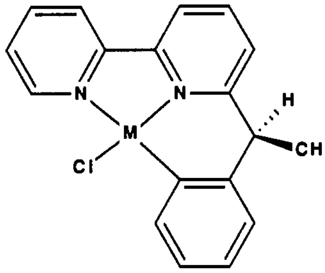
© Copyright 1990 by the American Chemical Society

Communications

Unusual Platinum Hydrides with Nitrogen Ligands

Most of the known platinum hydrides are stabilized by phosphine ligands.[1] Few of them also contain a Pt–N bond,[2] and fewer still have only nitrogen ligands. An example of the latter type is the dinuclear monohydrogen-bridged complex $\{Pt_2[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2(\mu\text{-}H)\}^+$, described by van Koten and coworkers, stabilized by a terdentate anionic ligand with an N–C–N sequence of donor atoms. The mononuclear hydride [Pt(N–C–N)H] was postulated as an intermediate but not isolated.[3]

We have reported previously[4] the synthesis of some six-membered cyclometalated derivatives of platinum(II) and palladium(II) derived from the chiral bipyridine 6-(1-methylbenzyl)-2,2′-bipyridine, e.g. I (M = Pt) and II (M = Pd), where the terdentate ligand is bonded to the metal through an N–N–C sequence.



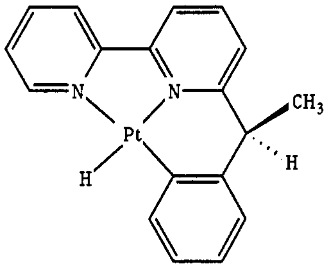
I M = Pt

II M = Pd

In complex II, [Pd(N–N–C)Cl], the six-membered cycle was shown by X-ray structure determination to adopt a boat conformation, with the CH_3 group directed toward the metal atom.

Here we report the isolation of complex III, [Pt(N–N–C)H], i.e. a platinum mononucler hydride stabilized by a heterocyclic nitrogen ligand.

Complex III[5] can be obtained either by reaction of I with excess $Na[BH_4]$ in alcoholic solution (eq 1) or by thermal CO_2 elimination from a stable formato species, [Pt(N-N-C)OC(O)H][6] (IV), which is likely to be an O-bonded derivative (eq 2).



III

$$[Pt(N\text{-}N\text{-}C)Cl] + Na[BH_4] \rightarrow [Pt(N\text{-}N\text{-}C)H] \quad (1)$$

$$[Pt(N\text{-}N\text{-}C)(S)]^+ + K[OC(O)H] \rightarrow$$
$$\underset{\text{IV}}{[Pt(N\text{-}N\text{-}C)(OC(O)H)]} \xrightarrow{\Delta} [Pt(N\text{-}N\text{-}C)H] + CO_2 \quad (2)$$

Complex III was characterized by elemental analysis and IR and ^1H NMR spectra. In the IR spectrum, a medium band at 2157 cm^{-1} in a Nujol mull (2153 cm^{-1}, $CHCl_3$) is assigned to the Pt–H stretch. The ^1H NMR spectrum (hydride region, $CDCl_3$, room temperature) shows a singlet at δ −13.56 flanked by satellites (1:4:1), $^1J_{Pt\text{-}H} = 1606$ Hz. As far as we know, this value is the largest ever reported for a platinum–hydrogen coupling. In an NMR tube, no H/D exchange is observed on shaking the chloroform solution with D_2O. Although minor signals are sometimes observed, the presence, in the ^1H NMR spectra, of one signal only for the CH_3 and CH protons indicates that one conformer is largely predominant in solution. As previously reported for complex I,[4] a small coupling to platinum is observed (80 MHz) for the CH_3 protons ($J_{Pt\text{-}H} = 4$ Hz), suggesting some kind of interaction of this group with the metal[7] and supporting a structure similar to that found for complex II.[8]

---

(1) (a) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

(2) (a) Gavrilova, I. V.; Gel'fman, M. I.; Razumovskii, V. V. *Russ. J Inorg. Chem.* (*Engl. Transl.*) **1974**, *19*, 1360. (b) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006. (c) Bayon, J. C.; Kolowich, J. B.; Rasmussen, P. G. *Polyhedron* **1982**, *1*, 57. (d) Cowan, R. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 2451. (e) Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3974.

(3) (a) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4285. (b) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoet, R.; Spek, A. L. *J. Organomet. Chem.* **1984**, *263*, C10.

(4) Minghetti, G.; Cinellu, M. A.; Chelucci, G.; Gladiali, S.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *307*, 107.

(5) Analytical data for III are as follows. Color: orange-red. Yield: 65%. Mp: 210–212 °C. Anal. Calcd for $C_{18}H_{16}N_2Pt$: C, 47.46; H, 3.51; N, 6.15. Found: C, 47.35; H, 3.69; N, 5.97. ^1H NMR ($CDCl_3$, room temperature, 300 MHz): δ −13.56 (s, $^1J_{Pt\text{-}H} = 1606$ Hz, 1:4:1, 1 H), 1.72 (d, $^3J_{H\text{-}H} = 7.0$ Hz, 3 H), 4.35 (q, $^3J_{H\text{-}H} = 7.0$ Hz, 1 H), 6.8–9.31 (m, 11 H).

(6) The solvato derivatives $[Pt(N\text{-}N\text{-}C)(S)][BF_4]$, where S is acetone or water, were obtained by reaction of I with $AgBF_4$ (molar ratio 1:1) in dry or moist acetone, respectively. Complex IV can be obtained under strictly controlled conditions, in acetone solution at room temperature in the presence of a large excess of potassium formate. Analytical data for IV are as follows. Color: orange. Yield: 80%. Mp: 162–163 °C. Anal. Calcd for $C_{19}H_{15}N_2O_2Pt$: C, 45.77; H, 3.01; N, 5.62. Found: C, 45.29; H, 3.44; N, 5.62. MW: calcd, *m/e* 498; found (FABMS, *o*-nitrobenzyl alcohol, $[MH]^+$), *m/e* 499. IR (Nujol; cm^{-1}): $\nu(CO_2)$ 1620 vs. ^1H NMR ($CDCl_3$, room temperature, 300 MHz): δ 1.68 (d, $^3J_{H\text{-}H} = 7.0$ Hz, 3 H), 4.17 (q, $^3J_{H\text{-}H} = 7.0$ Hz, 1 H), 6.9–9.5 (m, 11 H), 8.66 (s, $^3J_{Pt\text{-}H} = 91$ Hz, 1 H). From complex IV, CO_2 elimination to give III can be attained by treating a solid sample of IV under vacuum in a dry oven (ca. 150 °C) for several hours.

(7) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, *29*, 1812.

(8) Preliminary X-ray data indicate that even in complex I the six-membered cycle is in a boat conformation, the CH_3 group pointing toward the platinum atom. (Demartin, F. Personal communication.)

0020-1669/90/1329-5137$02.50/0 © 1990 American Chemical Society

On the whole, the IR and NMR data are in agreement with a Pt–H bond trans to a group of low trans influence, as expected for a *trans*-N–Pt–H arrangement.

The stability of complex III, in comparison with that of the [Pt(N–C–N)H] species cited by van Koten,[3] is likely to be related to such an arrangement. In platinum chemistry, strong trans directors such as H prefer weak trans-influence ligands (e.g. N donors) opposite to them.[9,2d]

In the attempt to verify the ability of the mononuclear hydrido complex to act as a donor,[10] complex III was reacted with a solvato species [Pt(N–N–C)(S)][BF$_4$] (V) (S = CH$_3$COCH$_3$, H$_2$O) (eqs 3 and 4). The reaction product analyzes correctly for the dinuclear derivative VI;[11] in agreement, the mass spectrum (positive ion, FAB conditions) shows the molecular ion [M$^+$] at *m/z* 909.

$$[\mathrm{Pt(N{-}N{-}C)Cl}] + \mathrm{AgBF_4} \xrightarrow{\mathrm{S}} \underset{\mathbf{V}}{[\mathrm{Pt(N{-}N{-}C)(S)}][\mathrm{BF_4}]} \qquad (3)$$

$$[\mathrm{Pt(N{-}N{-}C)H}] + [\mathrm{Pt(N{-}N{-}C)(S)}][\mathrm{BF_4}] \rightarrow \underset{\mathrm{VI}}{[\mathrm{(N{-}N{-}C)Pt}(\mu\text{-}\mathrm{H})\mathrm{Pt(N{-}N{-}C)}][\mathrm{BF_4}]} \qquad (4)$$

Whereas no evidence of a bridging hydride is given by the IR spectrum, this is proved unequivocally by the ^{1}H NMR spectrum. At room temperature (CD$_2$Cl$_2$), two signals are observed at δ −14.9 and at −15.95. For both signals the expected pattern (quintet, 1:8:18:8:1) is not fully resolved; however, the intensity ratio of the three central peaks (ca. 1:2:1) fits a dinuclear system. Once again the $J_{\mathrm{Pt-H}}$ values are large if compared with those observed in dinuclear platinum complexes with phosphorous ligands,[10a,b,12] as well as with those reported by van Koten.[3]

The presence of two signals (ca. 1:1, room temperature) in the hydrido region, taken together with the presence of more sets of signals for the protons of the organic ligand, supports the existence in solution of diastereoisomers. This is not surprising taking account of the complexity of a molecule, where the two [Pt(N–N–C)] moieties, each containing a six-membered cycle, are connected through the bridging hydrido. Further work is currently in progress to attain the separation of the isomers and their full characterization.

Although the palladium analogue of complex III has not been obtained from II, the isolation of the platinum hydride III may be relevant to the hypothesis that hydrido species are intermediates in reactions involving cyclopalladated molecules having nitrogen donors.[13]

Acknowledgment. Financial support by the MPI (Rome) and RAS (Regione Autonoma Sardegna) is gratefully acknowledged. We thank Mr. A. Canu (Università di Sassari) for the elemental analyses.

Dipartimento di Chimica
Università di Sassari
Sassari, Italy 07100

Giovanni Minghetti*
Maria Agostina Cinellu
Sergio Stoccoro
Giorgio Chelucci

Istituto per l'Applicazione delle
Tecniche Chimiche Avanzate ai
Problemi Agrobiologici del CNR
Sassari, Italy 07100

Antonio Zucca

Received August 8, 1990

---

(9) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(10) (a) Venanzi, M. L. *Coord. Chem. Rev.* **1982**, *43*, 251. (b) Knobler, C. B.; Kaesz, H. D.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1983**, *22*, 2324. (c) Chiang, M. Y.; Bau, R.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Koetzle, T. F. *Inorg. Chem.* **1984**, *23*, 122.

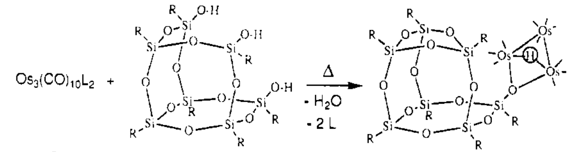
(11) Analytical data for IV are as follows: Color: orange-yellow. Yield: 70%. Dec pt: 205 °C. Anal. Calcd for C$_{36}$H$_{31}$BF$_4$N$_4$Pt$_2$: C, 43.37; H, 3.11; N, 5.62. Found: C, 42.77; H, 3.36; N, 5.64. ^{1}H NMR (CD$_2$Cl$_2$, room temperature, 300 MHz): δ −15.95 ($^1J_{\mathrm{Pt-H}}$ = 880 Hz, ca. 1:2:1, ca. 0.5 H), −14.9 ($^1J_{\mathrm{Pt-H}}$ = 936 Hz, ca. 1:2:1, ca. 0.5 H), 1.77 (d, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, ca. 1 H), [1.96 (d, $^3J_{\mathrm{H-H}}$ = 7.5 Hz) + 1.99 (d, $^3J_{\mathrm{H-H}}$ = 7.2 Hz), ca. 5 H], 4.60 (q, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, ca. 1 H), 4.67 (q, $^3J_{\mathrm{H-H}}$ = 7.5 Hz, ca. 0.5 H), 4.73 (q, $^3J_{\mathrm{H-H}}$ = 7.5 Hz, ca. 0.5 H), 6.7–10.8 (m, 22 H).

(12) (a) Minghetti, G.; Banditelli, G.; Bandini, A. L. *J. Organomet. Chem.* **1977**, *139*, C80. (b) Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F.; Szostak, R.; Strouse, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1983**, *22*, 2332. (c) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L27; *J. Chem. Soc., Dalton Trans.* **1978**, 516. (d) Tulip, T. H.; Yamagata, T.; Yoshida, T.; Wilson, R. D.; Ibers, J. A.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 2239.

(13) (a) Thompson, J. M.; Heck, R. *J. Org. Chem.* **1975**, *40*, 2667. (b) Albinati, A.; Pregosin, P. S.; Ruedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046.

A Triosmium Cluster–Siloxane Cage Complex. Synthesis and Structure of HOs$_3$(CO)$_{10}$[(μ-O)Si$_7$O$_{10}$(C$_6$H$_{11}$)$_7$]

Silica-supported metal species are technologically important catalysts, but the metal–silica interaction is difficult to define at the atomic level. One active approach to the problem is the preparation and characterization of molecular complexes incorporating M$_x$–O$_y$–Si$_z$ interactions as models for the catalytic materials.[1,2] Feher and co-workers[3] have shown that incompletely condensed silsesquioxane frameworks are effective models for silica surfaces. In view of the ongoing efforts to define the surface species formed from the interaction of M$_3$(CO)$_{12}$ (M = Os, Ru) with silica,[4-7] we have begun to examine the interaction of appropriate M$_3$(CO)$_{12}$ derivatives with silsequioxanes. In this paper we report the isolation and structural characterization of the triosmium–silsesquioxane complex (μ-H)Os$_3$(CO)$_{12}$[(μ-O)-Si$_7$O$_{10}$(C$_6$H$_{11}$)$_7$] (**1**), generated as shown in eq 1.



3 2 1 (1)

The reaction of the "lightly stabilized" cluster Os$_3$(CO)$_{10}$-(C$_8$H$_{14}$)$_2$ (**3**)[8] with the trisilanol (c-C$_6$H$_7$)$_7$Si$_7$O$_9$(OH)$_3$ (**2**)[3a] was conducted in cyclooctene at 130 °C for 24 h, and complex **1** was isolated as a stable, yellow solid in 13% yield following chromatography.[9] The formulation of **1** was established by using

---

(1) Iwasawa, Y., Ed. *Tailored Metal Catalysts*; Reidel: Boston, MA, 1986.

(2) Gates, B. C., Guczi, L., Knozinger, H., Eds. *Metal Clusters in Catalysis*; Elsevier: Amsterdam, 1986.

(3) (a) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741. (b) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931. (c) Feher, F. J.; Budzichowski, T. A. *Organometallics* (in press).

(4) Puga, J.; Fehlner, T. P.; Gates, B. C.; Braga, D.; Grepioni, F. *Inorg. Chem.* **1990**, *29*, 2376.

(5) Binsted, N.; Evans, J.; Greaves, G. N.; Price, R. J. *Organometallics* **1989**, *8*, 613.

(6) Walter, T. H.; Frauenhoff, G. R.; Shapley, J. R.; Oldfield, E. *Inorg. Chem.* **1988**, *27*, 2561.

(7) D'Ornelas, L.; Choplin, A.; Basset, J. M.; Hsu, J.-Y.; Shore, S. *Nouv. J. Chim.* **1985**, *9*, 155.

(8) Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *124*, C19.

(9) (C$_6$H$_{11}$)$_7$Si$_7$O$_9$(OH)$_3$ (73 mg, 0.075 mmol) was placed in a Schlenk tube, which was then evacuated (oil pump) for 20 min. A cyclooctene solution of Os$_3$(CO)$_{10}$(C$_8$H$_{14}$)$_2$ (80 mg, 0.075 mmol) was added under a nitrogen atmosphere, and the solution was heated in an oil bath at 130 °C for 24 h. The color turned from yellow to orange to brown. After removal of the solvent under reduced pressure, the residue was separated twice by preparative TLC (silica), eluting with a mixture of carbon tetrachloride/*n*-hexane (4:1). Several bands were separated, and the second fastest eluting yellow band corresponded to HOs$_3$(CO)$_{10}$[(μ-O)Si$_7$O$_{10}$(C$_6$H$_{11}$)$_7$] (17 mg, 13%). Single crystals of **1** were obtained from dichloromethane/*n*-hexane at −10 °C for 7 days. The other products resulting from this reaction have not been definitively formulated, although it is clear (^{1}H NMR, MS) that reaction(s) of the cyclooctene ligand(s) are involved. *Note*: Since this paper was submitted, we have found that Os$_3$(CO)$_{12}$ and **2** react slowly (117 h) in refluxing octane to give **1** as the major TLC-mobile product in 28% isolated yield.