Organometallics 1988, *7*, 1233–1234

New Ni(0)–CO-Monocoordinated Bis(phosphine) Complexes and Their Utility as Precursors of Heterobimetallic Systems: The Structure of $NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$

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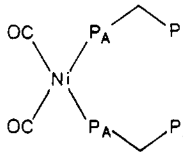
Received November 10, 1987

Summary: The syntheses and characterizations of $Ni(CO)_2(dppm\text{-}P)_2$ and Ni(CO)(diphos)(diphos-P), which contain monocoordinated bis(phosphine) ligands, are reported. The former reacts readily with $PtCl_2(COD)$ to give $NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$, the structure of which shows that each metal (1) is bonded to a terminal chloride and (2) has a different structure, the Pt being almost square planar while the Ni is considerably distorted from square planarity.

The most general synthetic route to the enormous number of transition metal–carbonyl–phosphine complexes now known is to react metal carbonyls with phosphines.[1] A less common approach is to treat either already substituted metal carbonyls[2] or metal(0) phosphine complexes[3] with CO. We report here an alternative route that involves the reaction of CO-saturated solutions of Ni(II)[4] (or Co(II)[5,6]) salts and phosphines, such as PPh_3 or $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, dppm; $n = 2$, diphos), with $NaBH_4$ or $NaBH_3CN$ under a variety of conditions, thereby avoiding the, sometimes inconvenient, use of metal carbonyls.

With PPh_3 and Ni(II), the major product is $Ni(CO)_2(PPh_3)_2$ (i.e., the same product as is observed[7] from reactions of $Ni(CO)_4$ with PPh_3), but with the bis(phosphines), hitherto unknown metal–CO–phosphine complexes containing monocoordinated phosphine ligands are produced. For example, the $NiCl_2{\cdot}6H_2O/dppm/CO/NaBH_4$ system yields[8] colorless crystals of tetrahedral $Ni(CO)_2(dppm\text{-}P)_2$ (1) which rapidly rearranges in solution (unless the solution is cooled or an excess of free dppm is present) to give $Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$.[4,9] Similar reactions using diphos instead of dppm produce[10] (along with other compounds) Ni(CO)(diphos)(diphos-P) (2).



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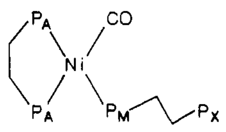

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There is obvious potential for the use of 1 and 2 in the synthesis of bimetallic systems,[11] and, indeed, 1 reacts very rapidly with, for example, $PtCl_2(COD)$, $NiCl_2{\cdot}6H_2O$, $Rh_2Cl_2(CO)_4$, and $Mo(CO)_5(THF)$ in CH_2Cl_2 under dry nitrogen. From 1 and $PtCl_2(COD)$, an intensely colored purple solution is produced from which purple crystals of $NiPtCl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ (3) have been isolated.[12] The structure of 3, solved by X-ray methods,[13] is shown in Figure 1, from which it is clear that the Ni and Pt atoms are each bonded to a terminal chlorine atom and are bridged by two dppm ligands and one carbonyl group. The metal, chlorine, and the carbonyl carbon atoms are essentially coplanar with the largest atom-to-plane distance from the least-squares plane through Pt, Ni, C1, Cl1, and Cl2 being 0.10 Å. The fact that P3 and P4 are approximately perpendicular to this plane and the P3–Pt–P4 and Cl2–Pt–C1 bond angles are 172.7° and 161.4°, respectively, indicate that the Pt atom is in an approximately square-planar environment. In contrast, the geometry about the Ni atom is considerably removed from square planarity, with P1–Ni–P2 and Cl1–Ni–C1 bond angles of 145.7° and

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(8) Ni salt:dppm:$NaBH_3CN$ ratio of 1:3:3.5, CO atmosphere, in C_6H_6/C_2H_5OH (1:1) at 20 °C for 2 h; product crystallized from the reaction filtrate; yield 40%. Anal. Calcd for $Ni(CO)_2(dppm)_2$: C, 70.69; H, 5.02. Found: C, 70.59; H, 5.22. IR (Nujol): ν (CO) 1992 (s), 1930 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR at 32.3 MHz: AA′XX′ pattern, δ_A 26.13, δ_X −23.74, $J_{AA'} = 16.50$, $J_{AX} = 108.25$, $J_{AX'} = 2.27$, $J_{XX'} = 0$ Hz. ^{31}P spectrum analyzed by the method of: Becker, E. D. *High Resolution NMR: Theory and Chemical Applications*, 2nd ed.; Academic: New York, 1981; pp 167–171 with assignments confirmed by a simulated spectrum using the Bruker ITRCAL program on a BNC 28 computer. Absolute signs for the coupling constants were not determined.

(9) Stanley, G. G.; Osborn, J. A.; Bird, P. H. *Abstracts of Papers, 190th National Meeting of the American, Chemical Society*, Chicago IL; American Chemical Society: Washington, DC, 1985; INOR-365. More recently, $Ni_2(CNMe)_3(dppm)_2$ has been shown to have a similar structure: DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1986**, *5*, 1807.

(10) Ni salt:diphos:$NaBH_3CN$ ratio of 1:3:3, CO atmosphere, in C_6H_6/C_2H_5OH (1:2) at 20 °C for 2 h; solid obtained by concentrating the reaction filtrate under reduced pressure; yield 90%. Anal. Calcd for $Ni(CO)(diphos)_2$: C, 72.05; H, 5.48. Found: C, 72.09; H, 5.66. $^{31}P\{^1H\}$ NMR at 32.3 MHz: A_2MX pattern, δ_A 43.96, δ_M 30.92, δ_X −12.20, $J_{AM} = 19.0$, $J_{AX} = 39.2$ Hz.

(11) For recent reviews, see: Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. Balch, A. L. In Homogeneous Catalysis with Metal Phosphine Complexes; Pignolet, L., ed.; Plenum: New York, 1983. See also the extensive work of Shaw and co-workers, e.g.: Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2751. Blagg, A.; Robson, R.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* 1987, 2171. Jacobsen, G. B.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1987**, 2005. Blagg, A.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 769. Fontaine, X. L. R.; Higgins, S. J.; Langrick, C. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1987**, 777. See also ref 15 below.

(12) $PtCl_2(COD)$:*1* ratio of 1:1 in CH_2Cl_2 at 20 °C; purple crystals precipitated over 2 days after adding C_2H_5OH; yield 25%. IR: ν (CO) (bridging) 1756 cm^{-1}. Anal. Calcd for $NiPtCl_2(CO)(dppm)_2{\cdot}0.33CH_2Cl_2$: C, 53.63; H, 3.92. Found: C, 53.72, H, 4.16.

(13) Crystal data: $C_{51}H_{44}Cl_2NiOP_4Pt$; M_r 1131.14; monoclinic; space group $P2_1/_n$; $a = 19.511$ (12) Å, $b = 18.122$ (9) Å, $c = 13.936$ (10) Å, $\beta = 99.72$ (5)°; $D_{calcd} = 1.47$ g cm^{-3}; $Z = 4$, $\lambda(Mo\ K\alpha) = 35.7$ cm^{-1}. A total of 5785 independent reflections with $I > 3\sigma(I)$] were collected (CAD-4 Enraf-Nonius diffractometer using Mo radiation) and used in the solution (Patterson) and refinement. Enraf-Nonius SDP programs were used in all calculations. Positional and thermal parameters for all non-hydrogen atoms were refined. All phenyl carbon atoms were refined isotropically; all other atoms were refined anisotropically. Hydrogen atoms were omitted. The crystal lattice contains a fractional amount of solvent, probably methylene chloride. Unfortunately, no satisfactory model could be found for this disordered solvent. The largest peak in the final difference-Fourier map, other than that attributed to disordered CH_2Cl_2, was 1.13 e A^{-3}. This peak is 0.27 Å from the Pt atom. Final R and R_w values are 0.069 and 0.106, respectively.

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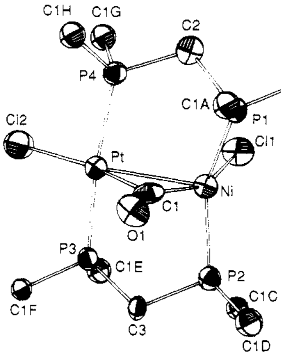

Figure 1. ORTEP of drawing of $[PtNi(\mu\text{-}CO)(\mu\text{-dppm})_2Cl_2]$ showing 50% probability thermal ellopsoids. For clarity, only phenyl carbons bonded to phosphorus atoms have been included. Selected bond lengths (Å): Pt-Ni, 2.689 (2); Pt-Cl2, 2.374 (5); Pt-C1, 2.03 (1); Pt-P3, 2.306 (4); Pt-P4, 2.323 (4); Ni-Cl1, 2.274 (4); Ni-C1, 1.77 (2); Ni-P1, 2.207 (4); Ni-P2, 2.209 (4); C1-O1, 1.22 (2). Bond angles (deg): P3-Pt-P4, 172.8 (1); P3-Pt-Cl2, 91.8 (2); P3-Pt-C1, 87.5 (4); P4-Pt-Cl2, 91.3 (2); P4-Pt-C1, 91.6 (4); Cl2-Pt-C1, 161.6 (5); P1-Ni-P2, 146.0 (2); P1-Ni-Cl1, 92.6(2); P1-Ni-C1, 87.1 (5); P2-Ni-Cl1, 105.8 (2); P2-Ni-C1, 90.5 (5); Cl1-Ni-C1, 149.9 (5); Pt-C1-Ni, 89.8 (6); Pt-C1-O1, 125 (1); Ni-C1-O1, 145 (1).

150.1°, respectively. The Pt-Pt distances in $Pt_2(\mu\text{-dppm})_2(\mu\text{-}HgCl_2)Cl_2$ and $Pt_2(\mu\text{-dppm})_2Cl_2$ are 2.712 and 2.651 Å, respectively.[14] The Pt-Ni distance of 2.689 (2) Å therefore implies the presence of metal-metal bonding which would be consistent with 18- and 16-electron counts on Ni(0) and Pt(II), respectively,[15] a formulation which is supported by the fact that **3** in CH_2Cl_2 reverts to $Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-dppm})_2$ and $PtCl_2$(dppm). The structure of **3** is quite different from that of the related compound $Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-dpam})_2$ (dpam = the arsenic analogue of dppm).[16]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Senate Research Committee of Lakehead University, and the University of Minnesota-Duluth Computer Center for their generous financial support of this work.

Registry No. **1**, 113894-20-5; **2**, 32423-72-6; **3**, 113894-21-6; $Ni(CO)_2(PPh_3)_2$, 13007-90-4; $Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-dppm})_2$, 106251-27-8; $PtCl_2$(COD), 12080-32-9; $Rh_2Cl_2(CO)_4$, 14523-22-9; $Mo(CO)_5$(THF), 53248-43-4; Ni, 7440-02-0; Pt, 7440-06-4.

Supplementary Material Available: Summary of crystal data, data collection parameters, and refinement details and tables of positional and thermal parameters and interatomic distances and bond angles (13 pages), a listing of observed and calculated structure factors for the X-ray structural analysis of $NiPtCl_2(\mu\text{-}CO)(\mu\text{-dppm})_2$ (58 pages). Ordering information is given on any current masthead page.

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[14] Sharp, P. R. *Inorg. Chem.* **1986**, *25*, 4185. Manojlovic-Muir, Lj.; Muir, K. W.; Solomun, T. *Acta Cryst.*, **1979**, *B35*, 1237.

[15] The Fe-Pt bond distance in $(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)PtBr_2$ is almost identical at 2.647 (4) Å. Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 3079.

[16] Brown, M. P.; Keith, A. N.; Manojlovic-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chim. Acta* **1979**, *34*, L 223.

Additions and Corrections

Richard G. Ball, Michael R. Burke, and Josef Takats*: Synthesis and Comparative Study of Iron Triad $M(CO)_4(\eta^2\text{-alkyne})$ Complexes (M = Fe, Ru, Os; Alkyne = Bis(trimethylsilyl)acetylene). **1987**, *6*, 1918–1924.

An error occurred in the reported coalescence temperature, T_c, and the corresponding $\Delta G^{\ddagger}{}_{T_c}$ for carbonyl scrambling in $Ru(CO)_4(\eta^2\text{-BTMSA})$ appearing in Table V. The correct values are T_c = −64 °C and $\Delta G^{\ddagger}{}_{Tc}$ = 9.0 kcal/mol. As a consequence, the trend in $\Delta G^{\ddagger}$ for carbonyl scrambling now should be Fe = Ru < Os. Furthermore, although the inverse relationship between $\Delta G^{\ddagger}$ and $\Delta\delta$ and $\Delta\nu_{CC}$, shown graphically in Figure 4, is still correct, the linear relationship between these properties as the metal is changed is no longer valid. Admittedly the consequences of the error in T_c are not insignificant; nevertheless, they do not adversely effect the major conclusions of the paper. In particular, the importance of both σ/π components of the metal alkyne interaction in this series of compounds is valid. The unexpectedly similar $\Delta G^{\ddagger}{}_{T_c}$ for carbonyl scrambling of the Fe and Ru compounds further emphasizes the special behavior of Ru and other second-row transition metals when compared to their first- and third-row congeners. We regret the error and the attendant changes.

Yan-Lung Shi, Yi-Ci Gao, Qi-Zhen Shi,* David L. Kershner, and Fred Basolo*: Oxygen Atom Transfer Reactions to Metal Carbonyls. Kinetics and Mechanism of CO Substitution Reactions of $M(CO)_6$ (M = Cr, Mo, W) in the Presence of $(CH_3)_3NO$. **1987**, *6*, 1528–1531.

Table V on page 1531 should be corrected as follows.

compd	nucleophile	T, °C	k, $M^{-1}\ s^{-1}$	ref
$Cr(CO)_6$	N_3^-	30.0	9.7×10^{-3}	12
	$PhCH_2MgCl$	27.0	0.053	13b
$Mo(CO)_6$	$PhCH_2MgCl$	27.0	0.091	13b
$W(CO)_6$	CN^-	95.0	5.2×10^{-3}	11b
	$PhCH_2MgCl$	27.0	0.108	13b
	Me_3NO	25.0	0.366	*a*

In the abstract and the text, $PhCH_2MgCl$ should replace $PhCH_2MgBr$.