Organometallics 1990, 9, 1576-1579

A Coordinatively Unsaturated Trinickel Cluster with a Fluxional Diphosphine Ligand and the Structure of $[Ni_3(\mu_3\text{-}CO)(\mu\text{-}Me_2PCH_2PMe_2)_4]^{2+}[Na(NCBH_3)_3]^{2-}$

George Ferguson,[*,1a] Michael C. Jennings,[1a] Hameed A. Mirza,[1b] and Richard J. Puddephatt[*,1b]

Departments of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and University of Western Ontario, London, Ontario, Canada N6A 5B7

Received October 20, 1989

The first coordinatively unsaturated trinickel complex, $[Ni_3(\mu_3\text{-}CO)(\mu\text{-}Me_2PCH_2PMe_2)_4]^{2+}[Na(BH_3CN)_3]^{2-}$, has been prepared and characterized crystallographically (crystal data: monoclinic, space group $P2_1/n$ (No. 14), $a = 12.606$ (5) Å, $b = 24.113$ (7) Å, $c = 14.469$ (4) Å, $\beta = 95.99$ (3)°, $V = 4374$ (5) Å^3, $Z = 4$, $R_1 = 0.029$). The nickel complex contains a distorted $Ni_3(\mu_3\text{-}CO)$ group and is fluxional, whereas the analogous platinum cluster is more distorted toward a $Pt_3(\mu_2\text{-}CO)$ group and is stereochemically rigid. The fluxionality of the nickel cluster involves apparent rotation of an axially bound μ-dmpm ligand with respect to the roughly planar $Ni_3(\mu\text{-dmpm})_3$ unit. The anion contains a sodium ion with approximately trigonal-planar stereochemistry.

Introduction

The chemistry of *triangulo*-M_3 clusters has developed in different ways when M = Ni compared to when M = Pd, Pt.[2] Thus, when M = Pd, Pt, the complexes are coordinatively unsaturated with 42-electron (e.g. $[M_3(\mu_2\text{-}CO)_3(PR_3)_3]$, $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$),[2,3] 44-electron (e.g. $[M_3(\mu_2\text{-}CO)_3(PR_3)_4]$,[2] $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3(PR_3)]^{2+}$),[3] or 46-electron (e.g. $[Pt_3(\mu_2\text{-}CO)(\mu\text{-dmpm})_4]^{2+}$)[4] configurations. However, when M = Ni, most examples are coordinatively saturated with 48e (e.g. $[Ni_3(CO)_6\{\mu_3\text{-}HC(PPh_2)_3\}]$,[5] $[Ni_3(\mu_3\text{-}CPh)(\eta\text{-}C_5H_5)_3]$)[2] or 49-53e (e.g. $[Ni_3(\mu_3\text{-}CO)_2(\eta\text{-}C_5H_5)_3]$, $[Ni_3(\mu_3\text{-}S)_2(\eta\text{-}C_5H_5)_3]$)[2,6] configurations. There are connections between Ni and Pt in the cluster anions derived from $[M_3(CO)_6]^{2-}$, but the parent is not known when M = Ni and there are interesting structural differences in the higher nuclearity clusters.[2,7] Therefore, the new discovery of Ni_3 complexes bridged by diphosphine ligands[8] offers an unusual opportunity to compare the structures and properties of analogous triangulo clusters of nickel and platinum. This paper reports the synthesis, structure, and fluxional behavior of the first coordinatively unsaturated trinickel cluster.

Results and Discussion

The complex $[Ni_3(\mu_3\text{-}CO)(\mu\text{-dmpm})_4][Na(NCBH_3)_3]$ (**1a**; dmpm = $Me_2PCH_2PMe_2$) was prepared by reduction of nickel(II) chloride with $Na[BH_3CN]$ in the presence of dmpm and CO. Large black crystals (smaller crystals are purple) formed in the reaction solution and proved suitable for X-ray structure determination. The cation $[Ni_3(\mu_3\text{-}CO)(\mu\text{-dmpm})_4]^{2+}$ could also be precipitated as the BPh_4^- (**1b**) and PF_6^- (**1c**) salts. Purple solutions of the cation **1** are easily oxidized by air, but the solid complexes are air-stable.

The structure of **1a** was determined crystallographically and is shown in Figure 1. Bond distances and angles are given in Table I, and fractional atomic coordinates are in Table II. The cation can be considered to contain a roughly planar $Ni_3(\mu\text{-dmpm})_3$ unit, with a μ_3-CO ligand and a μ_2-dmpm ligand axially bound on either side of the Ni_3 triangle. The overall cluster electron count is 46e, and this appears to be unique in Ni_3 clusters.[2,5,6] The center of coordinative unsaturation is clearly at Ni3, since the extra axially bound μ-dmpm ligand coordinates to Ni1 and Ni2. The Ni-Ni distances (Table I) are in the expected range for single bonds.[2,6,7] Coordinatively unsaturated clusters sometimes take part in metal-metal multiple bonding, but these Ni-Ni bond distances do not suggest such an effect since they are very similar to values in 48-electron Ni_3 clusters.[2,6,7] All nickel-carbonyl distances are in the bonding range, though the Ni3-C distance (2.028 (3) Å) is significantly longer than the other two Ni-C distances (Ni1-C = 1.916 (3) Å, Ni2-C = 1.906 (3) Å).

The anion also has an interesting structure containing a sodium ion trigonally coordinated to three cyanoborohydride ligands, with distances Na-N = 2.370 (4), 2.374 (4), 2.387 (3) Å (Figure 2). Most coordination compounds of sodium have coordination number 6, and although there are some with coordination number 3, they contain much more complex ligands than the present example.[9]

There are two major differences between the cation **1** and the analogous platinum cluster cation $[Pt_3(\mu_2\text{-}CO)(\mu\text{-dmpm})_4]^{2+}$ (**2**).[4] The major structural difference is that in **1** the carbonyl ligand is a distorted μ_3-CO species, whereas in **2** it is more distorted toward μ_2-CO, as shown

---

[1] (a) University of Guelph. (b) University of Western Ontario.

[2] For leading references, see: Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, England, 1982; Vol. 6, Chapter 37.7. Mingos, D. M. P.; Wardle, R. W. M. *Transition Met. Chem.* **1985**, *10*, 441. Eremko, N. K.; Mednikov, E. G.; Kurasov, S. S. *Russ. Chem. Rev.* (*Engl. Transl.* **1985**, *54*, 394. Clark, H. C.; Jain, V. K. *Coord. Chem. Rev.* **1984**, *55*, 151. Browning, C. S.; Farrar, D. H.; Gukathasan, R. R.; Morris, S. A. *Organometallics* **1985**, *4*, 1750. Yamamoto, Y.; Takahashi, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 2458. Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225. Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

[3] Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344. Bradford, A. M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 792.

[4] Ling, S. S. M.; Hadj-Bagheri, N.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 231. Bradford, A. M.; Puddephatt, R. J. *New J. Chem.* **1988**, *12*, 427.

[5] Osborn, J. A.; Stanley, G. G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1025.

[6] Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054 and references therein. However, a reviewer has carried out a database search in which 104 structures with 307 Ni-Ni bonds gave a mean Ni-Ni distance of 2.643 (±0.219 esd) Å.

[7] Ceriotti, A.; Chini, P.; Pergola, R. D.; Longoni, G. *Inorg. Chem.* **1983**, *22*, 1595. Underwood, D. J.; Hoffmann, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968.

[8] Kubiak and co-workers have independently prepared and characterized the complex cation $[Ni_3(\mu_3\text{-}CNMe)(\mu_3\text{-}I)(CNMe)_2(\mu\text{-dppm})_2]^+$: Kubiak, C. P., Personal communication.

[9] Fenton, D. E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 3, Chapter 23. Chan, A. S. C.; Shieh, H.-S.; Hill, J. R. *J. Organomet. Chem.* **1985**, *279*, 171.

0276-7333/90/2309-1576\$02.50/0

Table I. Molecular Dimensions

(a) Bond Lengths (Å)

Ni1–Ni2	2.4596 (5)	Ni3–P7	2.2004 (8)	P4–C41	1.822 (3)	P8–C81	1.810 (3)
Ni1–Ni3	2.3756 (5)	Ni3–C	2.028 (3)	P4–C42	1.828 (3)	P8–C82	1.821 (4)
Ni1–P1	2.2119 (8)	P1–C1	1.832 (3)	P5–C3	1.830 (3)	O–C	1.189 (3)
Ni1–P3	2.2589 (8)	P1–C11	1.807 (4)	P5–C51	1.803 (4)	Na–N91	2.387 (3)
Ni1–P8	2.2043 (8)	P1–C12	1.815 (4)	P5–C52	1.814 (4)	Na–N92	2.374 (4)
Ni1–C	1.916 (3)	P2–C1	1.820 (3)	P6–C3	1.830 (3)	Na–N93	2.370 (4)
Ni2–Ni3	2.4360 (4)	P2–C21	1.809 (4)	P6–C61	1.804 (4)	N91–C91	1.134 (4)
Ni2–P2	2.2172 (8)	P2–C22	1.817 (3)	P6–C62	1.818 (4)	C91–B91	1.561 (6)
Ni2–P4	2.2544 (8)	P3–C2	1.817 (3)	P7–C4	1.829 (3)	N92–C92	1.126 (5)
Ni2–P5	2.1958 (9)	P3–C31	1.829 (3)	P7–C71	1.814 (4)	C92–B92	1.567 (7)
Ni2–C	1.906 (3)	P3–C32	1.822 (4)	P7–C72	1.824 (3)	N93–C93	1.138 (5)
Ni3–P6	2.1828 (9)	P4–C2	1.834 (3)	P8–C4	1.828 (3)	C93–B93	1.545 (6)

(b) Bond Angles (deg)

Ni2–Ni1–Ni3	60.47 (1)	P4–Ni2–P5	103.96 (3)	Ni1–P3–C32	121.0 (1)	C71–P7–C72	102.6 (2)
Ni2–Ni1–P1	95.27 (3)	P4–Ni2–C	143.98 (9)	C2–P3–C31	101.8 (1)	Ni1–P8–C4	107.8 (1)
Ni2–Ni1–P3	95.56 (2)	P5–Ni2–C	103.39 (9)	C2–P3–C32	102.5 (2)	Ni1–P8–C81	118.4 (1)
Ni2–Ni1–P8	149.43 (3)	Ni1–Ni3–Ni2	61.47 (1)	C31–P3–C32	99.1 (2)	Ni1–P8–C82	119.8 (1)
Ni2–Ni1–C	49.76 (8)	Ni1–Ni3–P6	160.32 (3)	Ni2–P4–C2	112.7 (1)	C4–P8–C81	104.3 (2)
Ni3–Ni1–P1	154.65 (3)	Ni1–Ni3–P7	97.17 (2)	Ni2–P4–C41	116.5 (1)	C4–P8–C82	101.9 (2)
Ni3–Ni1–P3	85.74 (2)	Ni1–Ni3–C	50.82 (8)	Ni2–P4–C42	121.6 (1)	C81–P8–C82	102.5 (2)
Ni3–Ni1–P8	97.88 (2)	Ni2–Ni3–P6	98.85 (3)	C2–P4–C41	103.5 (2)	Ni1–C–Ni2	80.1 (1)
Ni3–Ni1–C	55.16 (8)	Ni2–Ni3–P7	156.36 (3)	C2–P4–C42	99.6 (2)	Ni1–C–Ni3	74.0 1(9)
P1–Ni1–P3	105.21 (3)	Ni2–Ni3–C	49.51 (8)	C41–P4–C42	100.1 (2)	Ni1–C–O	138.7 (2)
P1–Ni1–P8	101.21 (3)	P6–Ni3–P7	102.16 (3)	Ni2–P5–C3	111.6 (1)	Ni2–C–Ni3	76.4 (1)
P1–Ni1–C	104.52 (8)	P6–Ni3–C	117.46 (8)	Ni2–P5–C51	116.2 (1)	Ni2–C–O	137.6 (2)
P3–Ni1–P8	104.57 (3)	P7–Ni3–C	109.98 (8)	Ni2–P5–C52	119.3 (1)	Ni3–C–O	122.9 (2)
P3–Ni1–C	135.83 (8)	Ni1–P1–C1	112.7 (1)	C3–P5–C51	104.3 (2)	P1–C1–P2	111.6 (2)
P8–Ni1–C	100.79 (8)	Ni1–P1–C11	116.3 (1)	C3–P5–C52	101.6 (2)	P3–C2–P4	109.8 (2)
Ni1–Ni2–Ni3	58.06 (1)	Ni1–P1–C12	120.4 (1)	C51–P5–C52	101.9 (2)	P5–C3–P6	109.9 (2)
Ni1–Ni2–P2	97.80 (3)	C1–P1–C11	103.1 (2)	Ni3–P6–C3	112.4 (1)	P7–C4–P8	109.6 (2)
Ni1–Ni2–P4	95.91 (2)	C1–P1–C12	100.6 (2)	Ni3–P6–C61	114.1 (1)	N91–Na–N92	117.8 (1)
Ni1–Ni2–P5	148.88 (3)	C11–P1–C12	101.2 (2)	Ni3–P6–C62	120.2 (1)	N91–Na–N93	106.7 (1)
Ni1–Ni2–C	50.12 (8)	Ni2–P2–C1	106.4 (1)	C3–P6–C61	103.8 (2)	N92–Na–N93	111.6 (1)
Ni3–Ni2–P2	147.75 (3)	Ni2–P2–C21	117.8 (1)	C3–P6–C62	102.0 (2)	Na–N91–C91	174.2 (3)
Ni3–Ni2–P4	100.82 (2)	Ni2–P2–C22	122.5 (1)	C61–P6–C62	102.3 (2)	N91–C91–B91	179.2 (3)
Ni3–Ni2–P5	94.36 (2)	C1–P2–C21	104.8 (2)	Ni3–P7–C4	111.9 (1)	Na–N92–C92	164.3 (4)
Ni3–Ni2–C	54.05 (8)	C1–P2–C22	102.1 (2)	Ni3–P7–C71	113.5 (1)	N92–C92–B92	179.2 (4)
P2–Ni2–P4	102.88 (3)	C21–P2–C22	101.1 (2)	Ni3–P7–C72	121.6 (1)	Na–N93–C93	143.6 (3)
P2–Ni2–P5	100.75 (3)	Ni1–P3–C2	108.0 (1)	C4–P7–C71	103.4 (2)	N93–C93–B93	179.5 (4)
P2–Ni2–C	94.52 (8)	Ni1–P3–C31	121.5 (1)	C4–P7–C72	101.7 (2)		

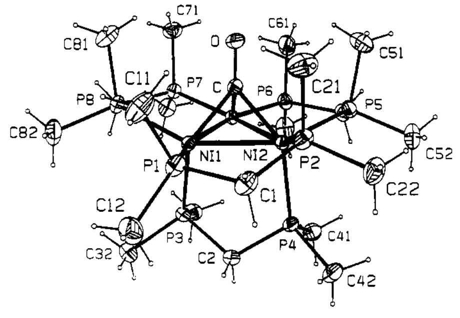

Figure 1. View of the cation $[Ni_3(\mu_3\text{-}CO)(\mu\text{-}dmpm)_4]^{2+}$. Ellipsoids are at the 25% level.

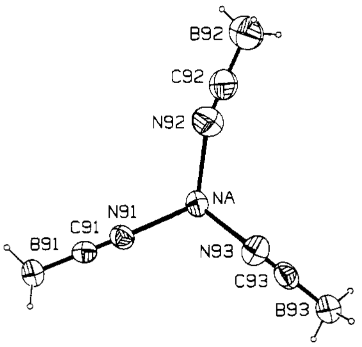

Figure 2. View of the anion $[Na(BH_3CN)_3]^{2-}$. Ellipsoids are at the 25% level.

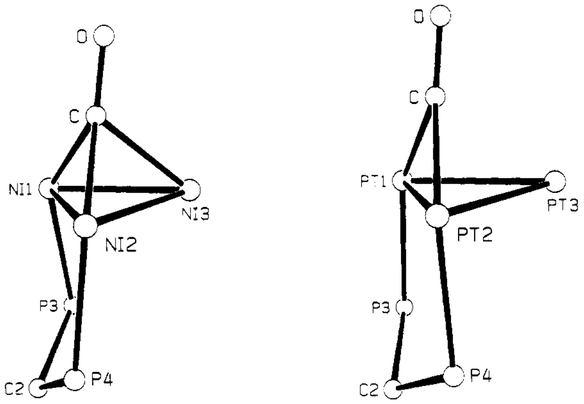

Figure 3. Comparison of the structures of the cations 1 and 2, with the equatorial dmpm ligands omitted for clarity. The Pt3–C distance of 2.47 (1) Å is 0.4 Å longer than the mean Pt1–C and Pt2–C distance and is too long for anything but a semibridging interaction.

in Figure 3.[4] The Pt3–C distance is 2.47 (1) Å, and the interaction with Pt3 is therefore weak. The carbonyl bends back away from Pt3 by only 6° in 2, whereas it bends away from Ni3 by 13° in 1, with respect to the M1M2C plane. Thus, the M3–CO bonding is much weaker in 2 than in 1, but a weak semibridging interaction is still possible. The carbonyl stretching frequencies for 1 and 2 are 1700 and 1730 cm^{-1}, respectively, consistent with a semibridging carbonyl in 2.[2] The second difference between 1 and 2 is that 1 is fluxional but 2 is not. Thus, while the NMR data for 2 at 25 °C are fully consistent with the structure determined crystallographically,[4] this is not the case for 1. The ^{31}P NMR spectrum for 1 at room temperature con-

Table II. Positional and Thermal Parameters and Their ESD's

atom	x	y	z	B,[a] Å^2
Ni1	0.20068 (3)	0.11033 (1)	0.78000 (2)	2.383 (6)
Ni2	0.13698 (3)	0.15314 (1)	0.91828 (2)	2.402 (6)
Ni3	0.01444 (3)	0.11993 (1)	0.78878 (2)	2.498 (6)
P1	0.37008 (6)	0.10705 (3)	0.83779 (6)	3.46 (2)
P2	0.28038 (7)	0.13694 (3)	1.01684 (6)	3.46 (2)
P3	0.18588 (6)	0.18784 (3)	0.69192 (5)	3.04 (1)
P4	0.16109 (6)	0.24158 (3)	0.87441 (5)	3.09 (2)
P5	0.01383 (7)	0.15914 (3)	1.01453 (5)	3.42 (2)
P6	−0.13594 (6)	0.14120 (4)	0.84238 (6)	3.51 (2)
P7	−0.03912 (6)	0.06790 (3)	0.66791 (5)	2.92 (1)
P8	0.19364 (6)	0.04169 (3)	0.67891 (5)	3.04 (1)
O	0.1083 (2)	0.03409 (8)	0.9060 (1)	3.70 (4)
C	0.1245 (2)	0.0786 (1)	0.8749 (2)	2.72 (5)
C1	0.3946 (2)	0.1424 (1)	0.9501 (2)	4.06 (7)
C2	0.2250 (3)	0.2466 (1)	0.7665 (2)	3.61 (6)
C3	−0.1160 (2)	0.1776 (1)	0.9538 (2)	3.77 (7)
C4	0.0709 (2)	0.0496 (1)	0.6007 (2)	3.39 (6)
C11	0.4254 (3)	0.0388 (2)	0.8617 (3)	6.1 (1)
C12	0.4724 (3)	0.1384 (2)	0.7754 (3)	5.78 (9)
C21	0.2930 (3)	0.0693 (2)	1.0709 (3)	5.50 (9)
C22	0.3196 (3)	0.1817 (2)	1.1155 (2)	4.77 (8)
C31	0.0571 (3)	0.2109 (1)	0.6349 (2)	4.17 (7)
C32	0.2666 (3)	0.1974 (2)	0.5958 (2)	4.85 (8)
C41	0.0413 (3)	0.2837 (1)	0.8510 (2)	4.34 (7)
C42	0.2455 (3)	0.2895 (1)	0.9471 (2)	4.78 (8)
C51	−0.0119 (3)	0.0969 (2)	1.0774 (3)	5.58 (9)
C52	0.0279 (3)	0.2104 (2)	1.1067 (2)	5.60 (9)
C61	−0.2164 (3)	0.0821 (2)	0.8663 (3)	6.06 (9)
C62	−0.2317 (3)	0.1857 (2)	0.7755 (3)	5.9 (1)
C71	−0.0913 (3)	0.0011 (1)	0.6989 (3)	4.89 (8)
C72	−0.1398 (3)	0.0920 (2)	0.5771 (2)	4.64 (8)
C81	0.1877 (3)	−0.0286 (1)	0.7218 (3)	4.74 (8)
C82	0.2939 (3)	0.0367 (2)	0.5974 (3)	5.55 (9)
Na	0.4230 (1)	0.08278 (6)	0.34852 (9)	4.60 (3)
N91	0.5318 (2)	0.0968 (1)	0.2251 (2)	4.32 (6)
C91	0.5870 (2)	0.1072 (1)	0.1705 (2)	3.61 (6)
B91	0.6642 (3)	0.1219 (2)	0.0964 (3)	4.93 (9)
N92	0.2579 (3)	0.1308 (2)	0.3410 (3)	7.4 (1)
C92	0.1746 (3)	0.1445 (2)	0.3514 (3)	5.61 (9)
B92	0.0591 (4)	0.1637 (3)	0.3673 (3)	7.4 (1)
N93	0.3992 (3)	−0.0143 (1)	0.3618 (2)	6.40 (9)
C93	0.4188 (3)	−0.0515 (2)	0.4089 (2)	4.64 (8)
B93	0.4442 (4)	−0.1021 (2)	0.4729 (3)	4.89 (9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

tains only two resonances, a triplet and septet with an intensity ratio of 3:1, respectively (Figure 4, J(PP) = 7 Hz). Thus, each of the phosphorus atoms P3 and P4 couples equally to the other six phosphorus atoms, implying rapid rotation of the axial dmpm ligand about the Ni_3 triangle, but without dissociation of this ligand from the cluster (Figure 4). At low temperature, this fluxionality was slower and the expected spectrum for the static structure **1** was obtained (Figure 4). In clusters of this kind, there is a large coupling ^3J(PP) for the roughly linear PMMP units.[3,4] In complex **1**, such couplings are $^3J(P^bP^b)$ and $^3J(P^aP^c)$ (Figure 4) and it follows that the singlet resonance at δ = −26.3 ppm is due to P^b while the "AB" doublets at δ = −29.2 and −32.6 ppm are due to P^a and P^c with ^3J(PP) = 138 Hz. The assignment of P^a and P^c to individual resonances is arbitrary and is based on a comparison with the spectrum of **2**, in which couplings to ^{195}Pt permit a more complete assignment.[4] The ^{31}P resonances are broad, at least partly due to the presence of unresolved PP couplings.

The fluxionality of **1** also leads to equivalence of the $CH^aH^bP_2$ and Me_2P protons of the axial dmpm ligand in the room-temperature ^{1}H NMR spectrum. The equatorial dmpm ligands give two resonances for the CH^aH^b and Me^aMe^bP protons, since these ligands are effectively equivalent due to the fluxionality, but this fluxional process does not lead to an effective plane of symmetry containing the Ni_3P_6 plane. The corresponding fluxionality of **2** would require a greater motion of the carbonyl ligand as well as the axial dmpm ligand, and so the structural difference between **1** and **2** could be a contributing factor to the higher activation energy for fluxionality of **2**. We note, however, that the complex $[Pt_3(\mu\text{-CO})(\mu\text{-dppm})_4]^{2+}$ (**3**; dppm = $Ph_2PCH_2PPh_2$) does exhibit fluxionality similar to that of **1** and that the fluxionality is not frozen out at −80 °C.[4] In complex **3** the fourth dppm ligand is weakly bound due to steric hindrance and the fluxionality is evidently faster due to this effect.[4]

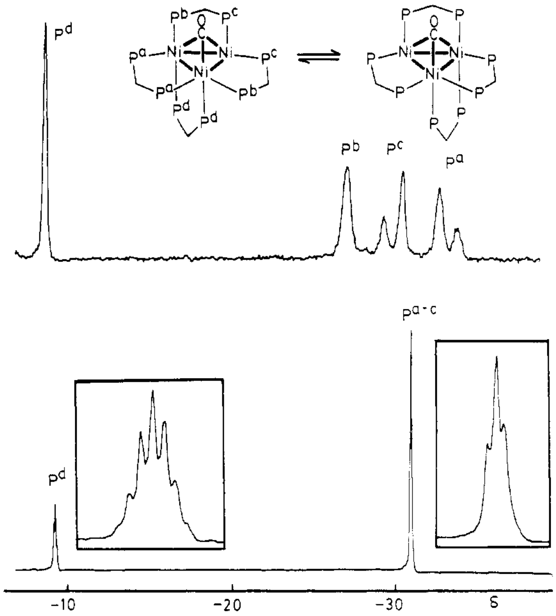

Figure 4. ^{31}P NMR spectra (121.5 MHz) of complex **1** at −80 °C (top) and at 21 °C (bottom) in methanol-d_4. The insets give expansions of the resonances at 21 °C to show the septet and triplet fine structure. The equation shows a 60° rotation of the dmpm ligand, P^dP^d; six such rotations are needed to give the observed equivalence of the ^{31}P atoms.

Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen. NMR spectra were recorded by using Varian XL200 (^{1}H, TMS reference) and XL300 (^{31}P, H_3PO_4 reference) NMR spectrometers. IR spectra were recorded by using a Bruker IFS 32 spectrophotometer.

$[Ni_3(\mu_3\text{-CO})(\mu\text{-dmpm})_4][Na(BH_3CN)_3]$. To a solution of $NiCl_2\cdot6H_2O$ (0.50 g, 2.10 mmol) in ethanol (30 mL) was slowly added $Me_2PCH_2PMe_2$ (1.18 g, 8.69 mmol), and the dark brown solution was stirred under a slow stream of CO for 0.5 h. A solution of $NaBH_3CN$ (0.50 g, 8.10 mmol) in ethanol (15 mL) was then added slowly (15 min), and the purple reaction mixture was stirred under CO for 2 h. The solution was filtered, the volume of solvent was reduced to ca. 7 mL, and the solution was layered with ether (10 mL) and allowed to stand at 0 °C for 1 week. The intensely purple crystals (large crystals appeared black) of the product that formed were washed with pentane and dried under vacuum: yield 35%; mp 203–204 °C. An analytical sample was obtained from CH_2Cl_2 and was shown by ^{1}H NMR spectroscopy to contain occluded CH_2Cl_2. Anal. Calcd for $C_{24}H_{65}B_3N_3NaNi_3OP_8\cdot CH_2Cl_2$: C, 30.8; H, 6.9; N, 4.3. Found, C, 29.6; H, 6.8; N, 4.6. IR (Nujol): ν(CO) 1700, 1688 cm^{-1}; ν(BH) and ν(CN) 2319, 2270, 2253, 2178, 2169 cm^{-1}. NMR at 25 °C in CD_3OD: ^{1}H, δ 3.07 (d, 3 H, ^2J(HH) = 14 Hz, $CH^aH^bP_2$), 2.89 (d, 3 H, ^2J(HH) = 14 Hz, $CH^aH^bP_2$), 2.56 (t, 2 H, ^2J(PH) = 10 Hz, $CH_2P^d{}_2$), 1.83 (12 H, MeP^d), 1.53, 1.39 (each 18 H, MeP^{a-c}), 1.84 (1:1:1:1 q, 6 H, ^1J(BH) = 88 Hz, BH_3CN); ^{31}P, δ −9.3 (septet, 2 P, ^2J(PP) = 7 Hz, P^d), −31.1 (t, 6 P, ^2J(PP) = 7 Hz, P^{a-c}); ^{31}P (at −80 °C), δ −7.9 (s, 2 P, P^d), −26.3 (s, 2 P, P^b), −29.2 (d, 2 P, ^3J(PP)

= 138 Hz, P^c), −32.6 (d, 2 P, $^3J(PP)$ = 138 Hz, P^a); ^{13}C (at −80 °C), δ 207.3 (s, CO). A limiting low-temperature ^1H NMR spectrum was not obtained at −90 °C, and the resonances were too broad to be useful.

$[Ni_3(\mu_3\text{-}CO)(\mu\text{-dmpm})_4][PF_6]_2$. To a solution of $[Ni_3(\mu_3\text{-}CO)(\mu\text{-dmpm})_4][Na(BH_3CN)_3]$ (0.3 g) in acetone (10 mL) was added excess NH_4PF_6 (0.2 g) in ethanol (8 mL). After 5 min, pentane (20 mL) was added to precipitate the product as a purple solid, which was washed with ether and pentane and dried under vacuum: yield 90%; mp 303–306 °C. Anal. Calcd for $C_{21}H_{56}F_{12}Ni_3OP_{10}$: C, 24.3; H, 5.4. Found: C, 23.9; H, 5.5. The NMR data for the cation were the same as for **1a**. IR: ν(CO) 1694 cm^{-1}; ν(^{13}CO) = 1645.5 cm^{-1} (obtained as a Nujol mull from a sample enriched in ^{13}CO).

X-ray Analysis of $[Ni_3(\mu_3\text{-}CO)(\mu\text{-dmpm})_4][Na(BH_3CN)_3]$. A crystal, grown as described above from ethanol/ether and having dimensions 0.50 × 0.50 × 0.60 mm, was mounted on a glass fiber for data collection in an Enraf-Nonius CAD4 diffractometer. The cell data and orientation matrix were determined from the setting angles of 25 reflections in the range $10° < \theta < 14°$. From the systematic absences ($h0l$, $h + l = 2n$; $0k0$, $k = 2n$) and from the subsequent least-squares refinement, the monoclinic space group was determined to be $P2_1/n$ (No. 14): a = 12.606 (5) Å, b = 24.113 (7) Å, c = 14.469 (4) Å, β = 95.99 (3)°, V = 4374 (5) Å^3, Z = 4, D_c = 1.35 g cm^{-3}, $F(000)$ = 1872, Mo Kα radiation (λ = 0.71073 Å), μ(Mo Kα) = 16.1 cm^{-1}. Intensity data (9952 reflections, 9524 unique reflections) were measured at 21 °C with use of the ω–2θ scan technique to a maximum of 2θ = 40.0°; Lorentz, polarization, decay (7.7% over the data collection), and an empirical absorption correction were applied to the data. The structure was solved with the aid of MULTAN, which gave the positions of the three nickel atoms and six phosphorus atoms. Full-matrix least-squares refinement, with hydrogens allowed as riding atoms, gave R_1 = 0.029 and R_2 = 0.038 for 6563 reflections with $I \geq 3\sigma(I)$. A final difference map revealed no chemically significant features. Scattering factors[10] and anomalous dispersion effects[11] were taken from the literature. All calculations were performed on a PDP-11 computer using SDP-PLUS.[12]

Acknowledgment. We thank the NSERC (Canada) for financial support.

Supplementary Material Available: Tables of experimental details, general temperature factors, calculated hydrogen coordinates, least-squares planes, and torsion angles (14 pages); a table of observed and calculated structure factors (66 pages). Ordering information is given on any current masthead page.

---

(10) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, Tables 2.2B and 2.3.1.

(11) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1974**, *17*, 781.

(12) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; p 64.

Synthesis, Structure, and Fluxionality of Clusters Formed by Addition of Bidentate Ligands to $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$): Structure of $[Pt_3(\mu\text{-}CO)(\mu\text{-dppm})_3(\mu\text{-}S_2CNMe_2)][PF_6]$

Arleen M. Bradford and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Graeme Douglas, Ljubica Manojlović-Muir, and Kenneth W. Muir

Chemistry Department, University of Glasgow, Glasgow, Scotland G12 8QQ

Received October 26, 1989

The 42-electron cluster cation $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**1**) reacts with bidentate ligands LL = $R_2NCS_2^-$ to give $[Pt_3(\mu\text{-}CO)(\mu\text{-dppm})_3(\mu\text{-}R_2NCS_2)]^+$ (**3a**, R = Me; **3b**, R = Et), with LL = R_3PCS_2 to give $[Pt_3(\mu\text{-}CO)(\mu\text{-dppm})_3(\mu\text{-}R_3PCS_2)]^{2+}$ (**3c**, R = Et; **3d**, R = cyclohexyl), and with LL = $R_2PCH_2PR_2$ to give $[Pt_3(\mu\text{-}CO)(\mu\text{-dppm})_3(\mu\text{-}R_2PCH_2PR_2)]^{2+}$ (**3e**, R = Me; **3f**, R = Ph). Complex **3a** has been shown by crystal structure analysis to contain the latitudinal $Pt_3(\mu\text{-dppm})_3$ core also present in **1**. However, the carbonyl ligand has slipped from a symmetrical μ_3-bonding mode found in **1** and now approximately doubly bridges the two platinum atoms that are also bridged by the dithiocarbamate ligand. The complexes **3a–d** and **3f** exhibit fluxionality of the added ligand LL, as shown by NMR spectroscopy.

Introduction

It has been established that monodentate phosphorus- and sulfur-containing ligands react readily with the coordinatively unsaturated, 42-electron cluster complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**1**)[1] to give 44-electron adducts such as $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3(PR_3)]^{2+}$ and $[Pt_3(SCN)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$.[2-4] Steric hindrance appears to prevent addition of more than one monodentate ligand except in the case of carbonyl, which can form the 46-electron complex $[Pt_3(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_3]^{2+}$.[5] The investigation of the reactions of **1** with bidentate ligands was of interest to find a more general route to unusual

---

(1) Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344.

(2) Bradford, A. M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 792.

(3) Bradford, A. M.; Douglas, G.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 409.

(4) Ferguson, G.; Lloyd, B. R.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4190.

(5) Lloyd, B. R.; Bradford, A. M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 424.

0276-7333/90/2309-1579$02.50/0