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Synthesis and Structure of the Cluster Cation $[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^+$

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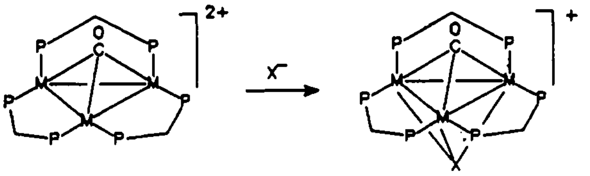
The cluster cation $[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$ (1), dppm = $Ph_2PCH_2PPh_2$, was prepared, as the chloride salt, by reaction of $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$ with $C_2H_4Cl_2$, by reaction of $[Ni_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]^+$ with CH_2Cl_2, or by heating $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ under vacuum. The structure of 1, as the BPh_4^- salt, characterized crystallographically, contains a triangular Ni_3 cluster with the edges spanned by three bridging dppm ligands and the faces capped by partially disordered μ_3-CO and μ_3-Cl ligands. The Ni–Ni bond lengths are 2.381 (1)–2.418 (1) Å. The crystals of $1[BPh_4]\cdot C_2H_4Cl_2$ are triclinic, space group $P\bar{1}$, a = 15.416 (1) Å, b = 15.676 (1) Å, c = 20.098 (2) Å, α = 68.146 (7)°, β = 89.008 (7)°, γ = 89.540 (6)°, Z = 2; the crystal structure, based on 6506 unique reflections with $I \geq 3\sigma(I)$, was refined to R = 0.035 and R_w = 0.041. The cation 1 completes the first triad of group 10 clusters, namely $[M_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^+$, where M = Ni, Pd, or Pt.

Introduction

The coordinatively unsaturated cluster cations $[M_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$, M = Pd or Pt, can add many small ligands in a way which often mimics chemisorption on a metal surface.[1] For example, as shown in eq 1, they add halide ions X^- to give the corresponding clusters $[M_3(\mu_3\text{-}X)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$.[1,2]



(1)

The analogous nickel complexes have not been reported, although there is a similar cluster $[Ni_3(\mu_3\text{-}I)(\mu_3\text{-}CNMe)(\mu\text{-}dppm)_3]^+$, and there appears to be no complete triad of nickel group clusters of any kind.[3] This papers reports the synthesis and structure of $[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$ (1) which completes the first triad of group 10 clusters, namely the cations $[M_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$, M = Ni, Pd and Pt.

Results

The formal oxidation state of the metal atoms in $[M_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ or $[M_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$ is $+^2/_3$ and there are a number of logical ways to prepare such complexes. For example, 2Ni(0) + Ni(II) or Ni(0) + 2Ni(I) might give 3Ni(2/3). A number of such reactions, for example $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$[4] with $[NiCl_2(dppm)]$, $[NiCl_2(dppm)_2]$,[5] or $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$[6] in the required ratio, were attempted unsuccessfully. The clusters $[M_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ with M = Pd or Pt are most easily prepared by reduction of $[M(O_2CCF_3)_2(dppm)]$ with CO/H_2O,[1] but this route was also unsuccessful when M = Ni. Finally, the cluster $[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]Cl$ was prepared by reaction of $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$[4] with refluxing 1,2-dichloroethane. This reaction uses the solvent 1,2-dichloroethane as both oxidant and source of chloride, according to eq 2. A similar reaction using 1,2-dibromoethane as oxidant was unsuccessful since more complete oxidation to nickel(II) appeared to occur.

$$3[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2] + 2C_2H_4Cl_2 \rightarrow 2[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]Cl + 2C_2H_4 \quad (2)$$

A similar preparation of $[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3][PF_6]$ was obtained by the slow decomposition of $[Ni_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2][PF_6]$ in dichloromethane, which occurs almost quantitatively. The complex 1Cl was also prepared by heating $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ briefly to 100 °C under vacuum. The intention was to drive off CO and form $[Ni_2Cl_2(\mu\text{-}dppm)_2]$, by analogy with the corresponding reactions when M = Pd or Pt,[7] but the only product was $1Cl^-$. A possible stoichiometry is shown in eq 3, though the volatile product was not characterized.

$$3[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2] \rightarrow 2[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]Cl + COCl_2 \quad (3)$$

Thus the trinuclear cation 1 can be prepared by mild oxidation of Ni(0) or mild reduction of Ni(I) but the experimental conditions are critical for success. For example, brominated or iodinated solvents appear to oxidize Ni(0) through to Ni(II) and so the desired clusters could not be obtained. The formation of trinuclear 1 from binuclear

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(1) For a review, see: Puddephatt, R. J.; Manojlović-Muir, Lj.; Muir, K. W. *Polyhedron* **1990**, *9*, 2767.

(2) (a) Manojlović-Muir, Lj.; Muir, K. W. Unpublished work. (b) Manojlović-Muir, Lj.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 536. (c) Lloyd, B. R.; Bradford, A.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 424. (d) Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344.

(3) Ratliff, K. S.; Fanwick, P. E.; Kubiak, C. P. *Polyhedron* **1990**, *9*, 1487.

(4) (a) Zhang, Z.-Z.; Wang, H.-K.; Wang, H.-G.; Wang, R.-J.; Zhao, W.-J.; Yang, L.-M. *J. Organomet. Chem.* **1988**, *347*, 269. (b) Osborn, J. A.; Stanley, G. G.; Bird, P. H. *J. Am. Chem. Soc.* **1988**, *110*, 2117. (c) Holah, D. G.; Hughes, A. N.; Mirza, H. A. *Inorg. Chim. Acta* **1987**, *126*, L7.

(5) Booth, G.; Chatt, J. *J. Chem. Soc.* **1965**, 3238.

(6) (a) Gong, J. K.; Morgenstern, D.; Fanwick, P. E.; Kubiak, C. P. *Abstracts of Papers*, 198th National Meeting of the American Chemical Society; American Chemical Society: Washington, DC 1989. (b) Manojlović-Muir, Lj.; Muir, K. W.; Davis, W. M.; Mirza, H. A.; Puddephatt, R. J. *Inorg. Chem.* **1992**, *31*, 904.

(7) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889 and references therein.

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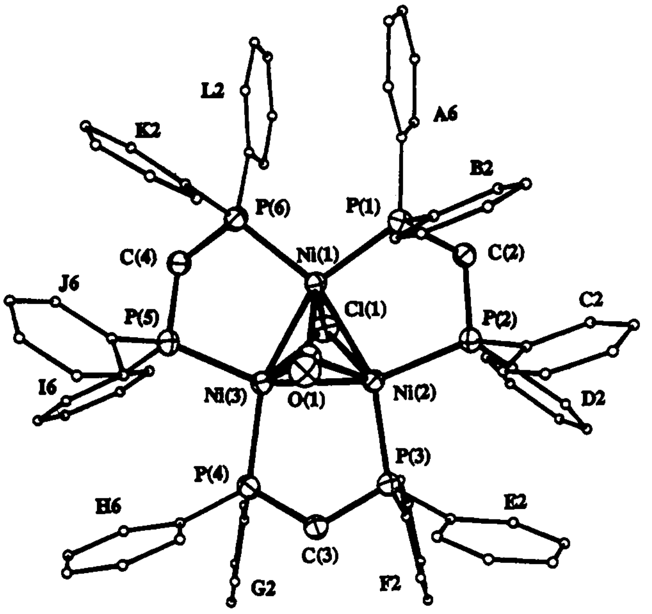

Figure 1. View of the structure of 1, in which the disordered μ_3-CO and μ_3-Cl ligands are shown in the arrangement with occupancy factor of 0.70 (2). In the phenyl rings the atoms are numbered cyclically, C(n1) to C(n6), where n = A, B, C, D, E, F, G, H, I, J, K, or L, and the C(n1) atom is bonded to phosphorus. For clarity, only the C(n2) atoms are labeled.

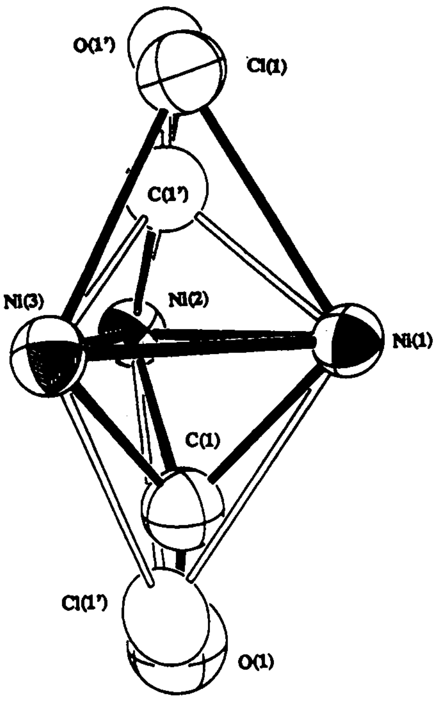

Figure 2. View of the $[Ni_3(\mu_3\text{-}CO)(\mu_3\text{-}Cl)]^+$ fragment illustrating the disorder of the CO and Cl ligands. The atomic occupancy factors are α [0.70 (2)] for C(1), O(1), and Cl(1) and $1 - \alpha$ for C(1'), O(1'), and Cl(1').

precursors clearly requires cleavage and re-formation of Ni–Ni and Ni–P bonds, and the detailed mechanisms remain obscure. Once formed, the cluster 1 is thermally stable and is mildly air sensitive.

The reaction product, $1Cl^-$, was crystallized from a dichloroethane/pentane mixture in the presence of $NaBPh_4$, and the identity of the product was then established by an X-ray diffraction study of $1[BPh_4]\cdot C_2H_4Cl_2$.

In the crystal structure of the salt, the solvent molecules $C_2H_4Cl_2$ are loosely entrapped in what would have been voids and their relatively high atomic displacement parameters suggest that they may be somewhat disordered. The geometry of the $[BPh_4]^-$ ions is as expected [B–C 1.631 (9)–1.654 (9) Å, C–B–C 104.0 (5)–112.7 (5)°].

The structure of the cationic cluster 1, shown in Figure 1, is closely similar to those of the complexes $[Pd_3(\mu_3\text{-}X)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$, X = Cl or I,[1,2] and $[Ni_3(\mu_3\text{-}I)(\mu_3\text{-}CNMe)(\mu\text{-dppm})_3]^+$.[3] It contains a triangular Ni_3 cluster, with Ni–Ni distances [2.381 (1)–2.418 (1) Å] indicative of nickel–nickel single bonds (2.37–2.69 Å).[3-6] The edges of the Ni_3 triangle are bridged by three dppm ligands to form a roughly planar $[Ni_3P_6]^{2+}$ skeleton, with the Ni–P bond lengths [2.195 (2)–2.214 (2) Å] lying within the range of those previously observed (2.18–2.26 Å).[3,8,9] The capping sites above the opposite faces of the Ni_3 cluster are occupied by triply bridging Cl and CO ligands, forming a distorted-trigonal-bipyramidal $[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)]^+$ unit. Close similarity of 1 with its palladium analogue, $[Pd_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$,[1,2b] extends to the observed Cl/CO disorder, each ligand spanning the capping sites on both sides of the Ni_3 cluster (Figure 2). The two resulting orientations of the $[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)]^+$ unit occur with 70:30 occupancy. Although the accuracy of the bond lengths and angles in the $[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)]^+$ unit (Table I) is somewhat lowered by the Cl/CO disorder, the Ni–C distances [1.82 (4)–1.96 (2) Å] are in accord with those (1.77–2.03 Å) found in the $[Ni_3(\mu_3\text{-}CO)(\mu\text{-}Me_2PCH_2PMe_2)_4]^{2+}$ cluster and in some carbonyl-bridged binuclear complexes.[4,6,10] The Ni–Cl distances [2.50 (2)–2.69 (3) Å] can be compared with long Ni–Cl bonds of 2.527 (2) Å in $[NiCl_2(dppm)_2]$[11] and 2.699 (7) Å in $[NiCl(CH_2\{CH_2P(Ph)CH_2CH_2CH_2NH_2\}_2)]$,[12] but they are substantially longer than the distances (2.22–2.27 Å) considered typical of normal covalent Ni–Cl bonds.[6,10,13] In the closely related complexes $[Pd_3(\mu_3\text{-}X)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$, X = Cl or I, and $[Ni_3(\mu_3\text{-}X)(\mu_3\text{-}CNMe)(\mu\text{-dppm})_3]^+$, X = I, the metal–halogen bonds are also abnormally long (Pd–Cl 2.74–3.16, Pd–I 2.95–3.03, Ni–I 2.73–2.78 Å).[1-3] It thus appears that weak covalent character of the $M_3(\mu_3\text{-}X)$ interaction is a common feature of the halogen adducts of the $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (M = Ni or Pd) and $[Ni_3(\mu\text{-}CNMe)(\mu\text{-dppm})_3]^{2+}$ clusters.

In 1 and in the other crystallographically characterized $[M_3(\mu_3\text{-}X)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^+$ complexes (M = Pd, X = Cl^-, I^-, or CF_3COO^-; M = Pt, X = SnF_3^-),[1,2,14,15] the three M_2P_2C rings adopt envelope shapes, two with the CH_2 groups at the flaps lying above and the third with the CH_2 group at the flap lying below the M_3P_6 plane. Thus one

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(8) (a) De Laet, D. L.; Powell, D. R.; Kubiak, C. P. *Organometallics* **1985**, *4*, 954. (b) De Laet, D. L.; del Rosario, R.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1987**, *109*, 754. (c) Gong, J.; Huang, J.; Fanwick, P. E.; Kubiak, C. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 396. (d) Ratliff, K. S.; Broeker, G. K.; Fanwick, P. E.; Kubiak, C. P. *Ibid.* **1990**, *29*, 395.

(9) De Laet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1986**, *5*, 1807.

(10) (a) Ferguson, G.; Jennings, M. C.; Mirza, H. A.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 1576. (b) Holah, D. G.; Hughes, A. N.; Magnuson, V. R.; Mirza, H. A.; Parker, K. O. *Organometallics* **1988**, *7*, 1233. (c) Schreiner, S.; Setzer, M. M.; Gallaher, T. N. *Inorg. Chim. Acta* **1991**, *188*, 131.

(11) Manojlović-Muir, Lj.; Mirza, H. A.; Puddephatt, R. J.; Sadiq, N. *Inorg. Chem.*, in press.

(12) Scanlon, L. G.; Tsao, Y.-Y.; Toman, K.; Cummings, S. C.; Meek, D. W. *Inorg. Chem.* **1982**, *21*, 2707.

(13) Gong, J. K.; Fanwick, P. E.; Kubiak, C. P. *J. Chem. Soc., Chem. Commun.* **1990**, 1190.

(14) Manojlović-Muir, Lj.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1336.

(15) Douglas, G.; Jennings, M. C.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1989**, 159.

Table I. Selected Bond Lengths (Å) and Angles (deg) in $[Ni_3Cl(CO)(Ph_2PCH_2PPh_2)_3]^+$

Ni(1)–Ni(2)	2.400 (1)	Ni(1)–Ni(3)	2.418 (1)
Ni(1)–Cl(1)	2.497 (16)	Ni(1)–Cl(1′)	2.690 (28)
Ni(1)–P(1)	2.207 (2)	Ni(1)–P(6)	2.210 (2)
Ni(1)–C(1)	1.913 (15)	Ni(1)–C(1′)	1.900 (38)
Ni(2)–Ni(3)	2.381 (1)	Ni(2)–Cl(1)	2.605 (16)
Ni(2)–Cl(1′)	2.598 (30)	Ni(2)–P(2)	2.205 (2)
Ni(2)–P(3)	2.195 (2)	Ni(2)–C(1)	1.956 (15)
Ni(2)–C(1′)	1.847 (37)	Ni(3)–Cl(1)	2.563 (16)
Ni(3)–Cl(1′)	2.549 (32)	Ni(3)–P(4)	2.214 (2)
Ni(3)–P(5)	2.196 (2)	Ni(3)–C(1)	1.908 (16)
Ni(3)–C(1′)	1.819 (34)	P(1)–C(2)	1.838 (5)
P(1)–C(A1)	1.829 (5)	P(1)–C(B1)	1.824 (6)
P(2)–C(2)	1.833 (5)	P(2)–C(C1)	1.808 (6)
P(2)–C(D1)	1.819 (6)	P(3)–C(3)	1.828 (5)
P(3)–C(E1)	1.825 (6)	P(3)–C(F1)	1.816 (6)
P(4)–C(3)	1.832 (5)	P(4)–C(G1)	1.815 (6)
P(4)–C(H1)	1.822 (6)	P(5)–C(4)	1.830 (5)
P(5)–C(I1)	1.822 (5)	P(5)–C(J1)	1.810 (6)
P(6)–C(4)	1.830 (5)	P(6)–C(K1)	1.814 (6)
P(6)–C(L1)	1.826 (6)	O(1)–C(1)	1.102 (37)
O(1′)–C(1′)	1.12 (9)		

Ni(2)–Ni(1)–Ni(3)	59.2 (1)	Ni(2)–Ni(1)–Cl(1)	64.2 (4)
Ni(2)–Ni(1)–Cl(1′)	61.1 (6)	Ni(2)–Ni(1)–P(1)	95.4 (1)
Ni(2)–Ni(1)–P(6)	156.2 (1)	Ni(2)–Ni(1)–C(1)	52.5 (4)
Ni(2)–Ni(1)–C(1′)	49.2 (12)	Ni(3)–Ni(1)–Cl(1)	62.8 (4)
Ni(3)–Ni(1)–Cl(1′)	59.6 (6)	Ni(3)–Ni(1)–P(1)	154.6 (1)
Ni(3)–Ni(1)–P(6)	98.6 (1)	Ni(3)–Ni(1)–C(1)	50.7 (5)
Ni(3)–Ni(1)–C(1′)	48.0 (10)	Cl(1)–Ni(1)–P(1)	110.0 (4)
Cl(1)–Ni(1)–P(6)	99.1 (4)	Cl(1)–Ni(1)–C(1)	103.4 (6)
Cl(1′)–Ni(1)–P(1)	108.5 (6)	Cl(1′)–Ni(1)–P(6)	117.6 (5)
Cl(1′)–Ni(1)–C(1′)	95.7 (13)	P(1)–Ni(1)–P(6)	106.7 (1)
P(1)–Ni(1)–C(1)	114.0 (5)	P(1)–Ni(1)–C(1′)	118.2 (9)
P(6)–Ni(1)–C(1)	122.1 (4)	P(6)–Ni(1)–C(1′)	110.4 (11)
Ni(1)–Ni(2)–Ni(3)	60.8 (1)	Ni(1)–Ni(2)–Cl(1)	59.7 (4)
Ni(1)–Ni(2)–Cl(1′)	65.0 (6)	Ni(1)–Ni(2)–P(2)	98.6 (1)
Ni(1)–Ni(2)–P(3)	156.9 (1)	Ni(1)–Ni(2)–C(1)	50.9 (5)
Ni(1)–Ni(2)–C(1′)	51.1 (10)	Ni(3)–Ni(2)–Cl(1)	61.7 (4)
Ni(3)–Ni(2)–Cl(1′)	61.4 (6)	Ni(3)–Ni(2)–P(2)	157.4 (1)
Ni(3)–Ni(2)–P(3)	97.1 (1)	Ni(3)–Ni(2)–C(1)	51.1 (5)
Ni(3)–Ni(2)–C(1′)	49.0 (10)	Cl(1)–Ni(2)–P(2)	100.9 (4)
Cl(1)–Ni(2)–P(3)	118.1 (4)	Cl(1)–Ni(2)–C(1)	98.5 (6)
Cl(1′)–Ni(2)–P(2)	120.9 (6)	Cl(1′)–Ni(2)–P(3)	99.5 (5)
Cl(1′)–Ni(2)–C(1′)	100.2 (13)	P(2)–Ni(2)–P(3)	104.2 (1)
P(2)–Ni(2)–C(1)	124.7 (4)	P(2)–Ni(2)–C(1′)	111.7 (10)
P(3)–Ni(2)–C(1)	111.0 (4)	P(3)–Ni(2)–C(1′)	120.8 (10)
Ni(1)–Ni(3)–Ni(2)	60.0 (1)	Ni(1)–Ni(3)–Cl(1)	60.1 (4)
Ni(1)–Ni(3)–Cl(1′)	65.5 (5)	Ni(1)–Ni(3)–P(4)	157.2 (1)
Ni(1)–Ni(3)–P(5)	96.5 (1)	Ni(1)–Ni(3)–C(1)	50.8 (5)
Ni(1)–Ni(3)–C(1′)	50.9 (11)	Ni(2)–Ni(3)–Cl(1)	63.5 (4)
Ni(2)–Ni(3)–Cl(1′)	63.5 (6)	Ni(2)–Ni(3)–P(4)	98.4 (1)
Ni(2)–Ni(3)–P(5)	156.1 (1)	Ni(2)–Ni(3)–C(1)	52.9 (4)
Ni(2)–Ni(3)–C(1′)	50.0 (12)	Cl(1)–Ni(3)–P(4)	119.3 (4)
Cl(1)–Ni(3)–P(5)	102.1 (4)	Cl(1)–Ni(3)–C(1)	101.3 (6)
Cl(1′)–Ni(3)–P(4)	99.5 (5)	Cl(1′)–Ni(3)–P(5)	113.3 (6)
Cl(1′)–Ni(3)–C(1′)	102.8 (14)	P(4)–Ni(3)–P(5)	105.5 (1)
P(4)–Ni(3)–C(1)	111.5 (5)	P(4)–Ni(3)–C(1′)	122.3 (10)
P(5)–Ni(3)–C(1)	117.5 (4)	P(5)–Ni(3)–C(1′)	112.8 (11)
Ni(1)–Cl(1)–Ni(2)	56.1 (4)	Ni(1)–Cl(1)–Ni(3)	57.1 (4)
Ni(2)–Cl(1)–Ni(3)	54.9 (4)	Ni(1)–Cl(1′)–Ni(2)	53.9 (6)
Ni(1)–Cl(1′)–Ni(3)	54.9 (7)	Ni(2)–Cl(1′)–Ni(3)	55.1 (7)
Ni(1)–P(1)–C(2)	107.0 (2)	Ni(1)–P(1)–C(A1)	122.0 (2)
Ni(1)–P(1)–C(B1)	117.7 (2)	Ni(2)–P(2)–C(2)	108.9 (2)
Ni(2)–P(2)–C(C1)	119.2 (2)	Ni(2)–P(2)–C(D1)	113.7 (2)
Ni(2)–P(3)–C(3)	110.0 (2)	Ni(2)–P(3)–C(E1)	116.2 (2)
Ni(2)–P(3)–C(F1)	118.2 (2)	Ni(3)–P(4)–C(3)	108.6 (2)
Ni(3)–P(4)–C(G1)	118.8 (2)	Ni(3)–P(4)–C(H1)	117.5 (2)
Ni(3)–P(5)–C(4)	108.3 (2)	Ni(3)–P(5)–C(I1)	118.3 (2)
Ni(3)–P(5)–C(J1)	117.5 (2)	Ni(1)–P(6)–C(4)	107.7 (2)
Ni(1)–P(6)–C(K1)	121.3 (2)	Ni(1)–P(6)–C(L1)	118.8 (2)
Ni(1)–C(1)–Ni(2)	76.7 (6)	Ni(1)–C(1)–Ni(3)	78.5 (7)
Ni(1)–C(1)–O(1)	138.9 (18)	Ni(2)–C(1)–Ni(3)	76.1 (6)
Ni(2)–C(1)–O(1)	128.8 (19)	Ni(3)–C(1)–O(1)	133.6 (17)
Ni(1)–C(1′)–Ni(2)	79.7 (17)	Ni(1)–C(1′)–Ni(3)	81.1 (15)
Ni(1)–C(1′)–O(1′)	127.7 (51)	Ni(2)–C(1′)–Ni(3)	81.0 (17)
Ni(2)–C(1′)–O(1′)	135.5 (50)	Ni(3)–C(1′)–O(1′)	131.6 (52)
P(1)–C(2)–P(2)	108.3 (3)	P(3)–C(3)–P(4)	108.9 (3)
P(5)–C(4)–P(6)	110.4 (3)		

Table II. Crystallographic data for $1[BPh_4]\bullet C_2H_4Cl_2$

empirical formula	$C_{102}H_{90}BCl_3Ni_3OP_6$
fw	1810.9
space group	$P\bar{1}$
a (Å)	15.416 (1)
b (Å)	15.676 (1)
c (Å)	20.098 (2)
α (deg)	68.146 (7)
β (deg)	89.008 (7)
γ (deg)	89.540 (6)
V (Å^3)	4507.2 (7)
Z	2
F(000) (electrons)	1880
d_{calc} (g cm^{-3})	1.334
cryst dimens (mm)	0.25 × 0.35 × 0.50
temp (°C)	23
radiation [wavelength (Å)]	Mo Kα (0.71069)
μ(Mo Kα) (cm^{-1})	8.64
data collcn range [2θ (deg)]	4–44
abs factors (on F)	0.82–1.10
no. of unique reflections with $I \geq 3\sigma(I)$	6506
no. of params refined	1053
R^a	0.035
$R_w{}^b$	0.041
largest peak in final ΔF map (e Å^{-3})	0.64

[a] $R = \sum ||F_o| - |F_c|| / |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$.

CH_2 group and four axial plus two equatorial phenyl groups form a fence around one face and two CH_2 groups and two axial plus four equatorial phenyl groups form a fence around the other face of the M_3P_6 skeletons (Figure 1). In such a conformation of the $[M_3(\mu\text{-dppm})_3]^{2+}$ fragment, the two faces of the M_3 cluster are exposed to sterically different environments, the steric hindrance being larger within the fence comprising four axial phenyl groups. The Cl/CO disorder observed in 1 and in its palladium analogue, resulting in two different orientations of the $[M_3(\mu_3\text{-Cl})(\mu_3\text{-CO})]^+$ unit with respect to the $[M_3(\mu_3\text{-dppm})_3]^{2+}$ skeleton, shows that small ligands, such as Cl and CO, can bind to either face of the M_3 cluster. The ligands of higher steric requirements, such as I^-, CF_3COO^-, and SnF_3^-, display a preference for the face of the M_3 cluster surrounded by the smaller number of axial phenyl groups.

The carbonyl stretching frequencies of $[M_3(\mu_3\text{-Cl})(\mu_3\text{-CO})(\mu\text{-dppm})_3]^+$ are 1717 (BPh_4^- salt), 1820 (PF_6^- salt), and 1767 (PF_6^- salt) cm^{-1} when M = Ni, Pd, and Pt, respectively. Hence back-bonding to CO is strongest for M = Ni and weakest for M = Pd, as is usual in this triad.

Experimental Section

$[Ni_3(\mu_3\text{-Cl})(\mu_3\text{-CO})(\mu\text{-dppm})_3]Cl$. A solution of $[Ni_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_2]$ (0.31 g) in $C_2H_4Cl_2$ (10 mL) was heated under reflux for 2 h. The color changed from orange to brown-black during this period. The solution was cooled to room temperature, and pentane (25 mL) was added to precipitate the product. Yield: 92%. Anal. Calc for $C_{76}H_{66}Cl_2Ni_3OP_6$: C, 63.9; H, 4.7. Found: C, 63.9; H, 4.7. IR (Nujol): ν(CO) = 1726 cm^{-1}. NMR in CD_2Cl_2: $\delta(^1H)$ = 3.86 (br s, CH_2P_2); $\delta(^{31}P)$ = −2.9 (s, dppm).

The same complex could be prepared by heating $[Ni_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ under vacuum at 100 °C for 5 min, followed by extraction into CD_3CN. The NMR and IR parameters were identical to those reported above.

$[Ni_3(\mu_3\text{-Cl})(\mu_3\text{-CO})(\mu\text{-dppm})_3]BPh_4$. To a solution of $[Ni_3(\mu_3\text{-Cl})(\mu_3\text{-CO})(\mu\text{-dppm})_3]Cl$ in $C_2H_4Cl_2$ (10 mL), prepared as above, was added $NaBPh_4$ (0.2 g) in ethanol (3 mL). This solution was layered with pentane (20 mL) and set aside for 2 weeks, after which time the black crystals of the product were filtered off and washed with cold ethanol and then ether. Anal. Calc for $C_{100}H_{86}BClNi_3OP_6$: C, 70.1; H, 5.0. Found: C, 69.5; H, 5.0. The NMR parameters were identical to those of the chloride salt listed above. IR (Nujol): ν(CO) = 1717 cm^{-1}.

Table III. Fractional Coordinates and Displacement Parameters (Å²) of Atoms[a]

	x	y	z	U
Ni(1)	0.00389 (4)	0.14597 (4)	0.22238 (3)	0.036
Ni(2)	−0.03856 (4)	−0.00896 (4)	0.24329 (3)	0.036
Ni(3)	−0.14519 (4)	0.10963 (4)	0.20847 (3)	0.038
Cl(1)	−0.031 (1)	0.113 (1)	0.113 (1)	0.057
Cl(1′)	−0.096 (1)	0.055 (2)	0.338 (2)	0.057
Cl(1S)	0.3029 (2)	0.2141 (2)	0.4521 (2)	0.203
Cl(2S)	0.5115 (2)	0.2091 (3)	0.4967 (2)	0.234
P(1)	0.14111 (8)	0.11267 (9)	0.25057 (7)	0.040
P(2)	0.09163 (8)	−0.07117 (9)	0.25223 (7)	0.040
P(3)	−0.12766 (8)	−0.12517 (9)	0.26542 (7)	0.041
P(4)	−0.26166 (8)	0.02246 (9)	0.22303 (7)	0.043
P(5)	−0.19333 (8)	0.25178 (9)	0.16776 (7)	0.041
P(6)	−0.00609 (8)	0.29752 (9)	0.17660 (7)	0.043
O(1)	−0.092 (2)	0.053 (2)	0.350 (2)	0.07 (1)
O(1′)	−0.035 (6)	0.112 (6)	0.102 (4)	0.04 (2)
C(1)	−0.0769 (8)	0.0712 (8)	0.2929 (9)	0.047 (4)
C(1′)	−0.048 (2)	0.095 (2)	0.161 (2)	0.048 (8)
C(2)	0.1724 (3)	0.0208 (3)	0.2188 (2)	0.042
C(3)	−0.2363 (3)	−0.0935 (3)	0.2862 (3)	0.047
C(4)	−0.1035 (3)	0.3276 (3)	0.1219 (3)	0.045
C(A1)	0.2280 (3)	0.1965 (3)	0.2127 (3)	0.047
C(A2)	0.2584 (4)	0.2474 (4)	0.2513 (3)	0.069
C(A3)	0.3241 (4)	0.3128 (4)	0.2225 (4)	0.087
C(A4)	0.3584 (4)	0.3265 (5)	0.1567 (5)	0.088
C(A5)	0.3295 (4)	0.2783 (5)	0.1177 (4)	0.085
C(A6)	0.2634 (4)	0.2129 (4)	0.1458 (3)	0.066
C(B1)	0.1681 (3)	0.0673 (3)	0.3454 (3)	0.045
C(B2)	0.2479 (3)	0.0249 (4)	0.3685 (3)	0.058
C(B3)	0.2665 (4)	−0.0088 (4)	0.4413 (3)	0.071
C(B4)	0.2075 (5)	−0.0004 (5)	0.4896 (3)	0.078
C(B5)	0.1292 (4)	0.0425 (5)	0.4678 (3)	0.080
C(B6)	0.1091 (3)	0.0757 (4)	0.3958 (3)	0.057
C(C1)	0.1307 (3)	−0.1427 (3)	0.3397 (3)	0.045
C(C2)	0.2114 (3)	−0.1863 (4)	0.3483 (3)	0.062
C(C3)	0.2393 (4)	−0.2362 (4)	0.4176 (4)	0.080
C(C4)	0.1901 (5)	−0.2423 (5)	0.4758 (4)	0.088
C(C5)	0.1114 (5)	−0.1969 (5)	0.4672 (3)	0.081
C(C6)	0.0820 (3)	−0.1479 (4)	0.3994 (3)	0.056
C(D1)	0.1090 (3)	−0.1359 (3)	0.1945 (3)	0.051
C(D2)	0.1219 (4)	−0.2306 (4)	0.2210 (3)	0.074
C(D3)	0.1211 (5)	−0.2768 (5)	0.1739 (5)	0.101
C(D4)	0.1094 (5)	−0.2330 (7)	0.1035 (5)	0.112
C(D5)	0.0987 (5)	−0.1389 (6)	0.0762 (4)	0.101
C(D6)	0.0992 (4)	−0.0902 (4)	0.1217 (3)	0.071
C(E1)	−0.1044 (3)	−0.2273 (3)	0.3444 (3)	0.047
C(E2)	−0.0504 (4)	−0.2955 (4)	0.3383 (3)	0.067
C(E3)	−0.0252 (5)	−0.3683 (4)	0.4007 (5)	0.096
C(E4)	−0.0552 (6)	−0.3741 (5)	0.4662 (4)	0.101
C(E5)	−0.1081 (5)	−0.3082 (5)	0.4728 (3)	0.095
C(E6)	−0.1326 (4)	−0.2344 (4)	0.4119 (3)	0.070
C(F1)	−0.1453 (3)	−0.1689 (3)	0.1948 (3)	0.051
C(F2)	−0.1950 (4)	−0.2467 (4)	0.2061 (3)	0.071
C(F3)	−0.2133 (5)	−0.2742 (5)	0.1503 (5)	0.101
C(F4)	−0.1821 (6)	−0.2237 (6)	0.0824 (5)	0.112
C(F5)	−0.1315 (6)	−0.1484 (5)	0.0714 (4)	0.107
C(F6)	−0.1143 (4)	−0.1206 (4)	0.1275 (3)	0.079
C(G1)	−0.3059 (3)	0.0062 (3)	0.1455 (3)	0.047
C(G2)	−0.3801 (3)	−0.0454 (4)	0.1499 (3)	0.065
C(G3)	−0.4122 (4)	−0.0548 (4)	0.0898 (4)	0.077
C(G4)	−0.3738 (4)	−0.0121 (5)	0.0251 (4)	0.097
C(G5)	−0.2999 (5)	0.0393 (6)	0.0191 (3)	0.116
C(G6)	−0.2664 (4)	0.0464 (5)	0.0802 (3)	0.086
C(H1)	−0.3570 (3)	0.0513 (3)	0.2654 (3)	0.051
C(H2)	−0.3653 (4)	0.0245 (4)	0.3386 (4)	0.076
C(H3)	−0.4357 (5)	0.0514 (5)	0.3712 (4)	0.095
C(H4)	−0.4972 (5)	0.1055 (6)	0.3301 (6)	0.108
C(H5)	−0.4905 (4)	0.1348 (5)	0.2564 (5)	0.105
C(H6)	−0.4207 (4)	0.1080 (4)	0.2244 (3)	0.073
C(I1)	−0.2712 (3)	0.2853 (3)	0.0953 (3)	0.045
C(I2)	−0.2471 (3)	0.2757 (4)	0.0319 (3)	0.072
C(I3)	−0.3018 (4)	0.3005 (5)	−0.0251 (3)	0.086
C(I4)	−0.3821 (4)	0.3356 (5)	−0.0206 (3)	0.082
C(I5)	−0.4073 (4)	0.3440 (5)	0.0413 (4)	0.089
C(I6)	−0.3532 (3)	0.3183 (4)	0.0999 (3)	0.062
C(J1)	−0.2379 (3)	0.2961 (4)	0.2324 (3)	0.050
C(J2)	−0.2579 (4)	0.2349 (4)	0.3004 (3)	0.067
C(J3)	−0.2954 (5)	0.2666 (6)	0.3501 (3)	0.094
C(J4)	−0.3112 (5)	0.3575 (6)	0.3335 (4)	0.102
C(J5)	−0.2895 (5)	0.4191 (5)	0.2673 (4)	0.089
C(J6)	−0.2535 (4)	0.3897 (4)	0.2157 (3)	0.069
C(K1)	−0.0214 (3)	0.3632 (4)	0.2335 (3)	0.058
C(K2)	−0.0343 (4)	0.4584 (4)	0.2033 (4)	0.096
C(K3)	−0.0546 (5)	0.5064 (5)	0.2490 (6)	0.126
C(K4)	−0.0647 (6)	0.4566 (8)	0.3195 (5)	0.126
C(K5)	−0.0474 (7)	0.3695 (6)	0.3500 (4)	0.129
C(K6)	−0.0264 (5)	0.3202 (4)	0.3048 (4)	0.097
C(L1)	0.0757 (3)	0.3629 (3)	0.1111 (3)	0.050
C(L2)	0.1328 (4)	0.4211 (4)	0.1250 (3)	0.078
C(L3)	0.1935 (5)	0.4705 (5)	0.0756 (5)	0.103
C(L4)	0.1987 (5)	0.4629 (5)	0.0103 (5)	0.095
C(L5)	0.1450 (5)	0.4060 (5)	−0.0053 (4)	0.090
C(L6)	0.0823 (4)	0.3535 (4)	0.0455 (3)	0.072
C(M1)	0.6365 (3)	0.4183 (4)	0.7049 (3)	0.058
C(M2)	0.6808 (4)	0.4193 (4)	0.6432 (4)	0.083
C(M3)	0.7632 (4)	0.4560 (5)	0.6238 (4)	0.087
C(M4)	0.8054 (4)	0.4955 (5)	0.6630 (4)	0.085
C(M5)	0.7644 (5)	0.4959 (5)	0.7233 (5)	0.108
C(M6)	0.6831 (4)	0.4577 (5)	0.7441 (3)	0.084
C(N1)	0.4986 (3)	0.3809 (5)	0.7979 (3)	0.064
C(N2)	0.4912 (4)	0.4687 (4)	0.8006 (3)	0.078
C(N3)	0.4484 (5)	0.4838 (6)	0.8573 (5)	0.107
C(N4)	0.4092 (5)	0.4115 (8)	0.9110 (5)	0.111
C(N5)	0.4131 (5)	0.3269 (7)	0.9100 (4)	0.103
C(N6)	0.4579 (4)	0.3119 (5)	0.8533 (4)	0.084
C(O1)	0.4692 (3)	0.4071 (4)	0.6655 (3)	0.057
C(O2)	0.4786 (4)	0.4834 (4)	0.6033 (3)	0.074
C(O3)	0.4125 (5)	0.5179 (5)	0.5541 (3)	0.082
C(O4)	0.3335 (4)	0.4758 (5)	0.5658 (4)	0.086
C(O5)	0.3198 (4)	0.4011 (6)	0.6264 (4)	0.093
C(O6)	0.3868 (4)	0.3673 (5)	0.6748 (3)	0.082
C(P1)	0.5622 (3)	0.2576 (4)	0.7440 (3)	0.056
C(P2)	0.5358 (4)	0.2111 (4)	0.7001 (3)	0.067
C(P3)	0.5555 (4)	0.1195 (5)	0.7137 (4)	0.084
C(P4)	0.6019 (4)	0.0693 (4)	0.7732 (4)	0.082
C(P5)	0.6313 (4)	0.1128 (5)	0.8164 (3)	0.071
C(P6)	0.6131 (4)	0.2042 (5)	0.8017 (3)	0.073
C(1S)	0.371 (1)	0.303 (1)	0.449 (1)	0.263
C(2S)	0.419 (1)	0.274 (1)	0.510 (1)	0.288
B	0.5418 (4)	0.3658 (5)	0.7277 (3)	0.058

[a] For O(1), O(1′), C(1), and C(1′) atoms U is the isotropic displacement parameter and for other atoms $U = {}^1/_3 \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} a_i^* a_j (\vec{a}_i \cdot \vec{a}_j)$.

$[Ni_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]PF_6$. A solution of $[Ni_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2][PF_6]$ (0.15 g) in CD_2Cl_2 (0.5 mL) was allowed to stand at room temperature for 4 days. NMR analysis indicated that >90% conversion to the product had occurred with $[Ni_2(CO)_4(\mu\text{-dppm})_2]$ as the only detectable impurity. The solvent was evaporated to give the product. The ^1H and ^{31}P NMR and IR parameters were identical to those of the authentic cation with the addition of peaks due to $[PF_6]^-$.

X-ray Crystal Structure Analysis of $[Ni_3(\mu_3\text{-}CO)(\mu_3\text{-}Cl)(\mu\text{-dppm})_3][BPh_4]\cdot C_2H_4Cl_2$, 1$[BPh_4]\cdot C_2H_4Cl_2$. All crystallographic measurements were made with graphite-monochromated molybdenum radiation, an Enraf-Nonius CAD4 diffractometer, and a fragment of a black crystal grown from a $C_2H_4Cl_2$/pentane mixture.

The unit cell dimensions (Table II) were determined by a least squares treatment of the diffractometric angles for 23 reflections with $12 \leq \theta \leq 16°$. The diffraction pattern revealed no systematic absence of reflections.

The intensities of reflections were measured by continuous $\theta/2\theta$ scans, with the width in θ of $(0.80 + 0.35 \tan \theta)°$. The scan speeds were adjusted to give $\sigma(1)(I) \leq 0.03$, subject to a time limit of 120 s. The integrated intensities of all reflections, derived in the usual manner ($q = 0.03$),[16] were corrected for Lorentz, polarization, and absorption effects, as well as for a linear drop (12.2%) in the intensities of two standard reflections remeasured every 2 h throughout the experiment. The absorption correction, made by an empirical method,[17] led to transmission factors on F of 0.82–1.10. Of 12 099 reflections measured, 2210 were related by symmetry and they were averaged to give 1105 independent ones and R(internal) of 0.023. Only unique reflections with $I \geq 3\sigma(I)$, of which there were 6505, were used in the structure analysis.

The structure was determined by the heavy atom method. The positions of the three nickel atoms were obtained from a Patterson function, and those of the remaining non-hydrogen atoms, as well as of a large number of hydrogen atoms, from the appropriate difference electron density maps. These maps also revealed that in the cationic complex the chloride and carbonyl ligands are disordered, each over two sites lying above opposite faces of the Ni_3 triangle (Figure 2). The disorder was accounted for by assigning occupancy parameters α to Cl(1), C(1), and O(1), and $1 - \alpha$ to Cl(1′), C(1′), and O(1′) atoms. The refinement of this parameter led to $\alpha = 0.70$ (2).

The structure was refined by a three-large-blocks approximation to the normal matrix, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(|F_o|)$. The carbon and oxygen atoms of the disordered carbonyl ligand were allowed isotropic displacement parameters, and all other non-hydrogen atoms anisotropic displacement parameters. In the final calculations the scattering of all 90 hydrogen atoms was accounted for by adding their fixed contribution to the structure factors; they were assigned a common isotropic displacement parameter, fixed at $U = 0.080$ Å^2, and their geometrically deduced positional parameters were constrained to C–H = 1.0 Å. The refinement converged at $R = 0.035$ and $R_w = 0.041$. In the final difference electron density map the highest peak was 0.64 e Å^{-3}. The residual electron density, mostly distributed in the vicinity of the solvent molecule, as well as its high atomic displacement parameters (Table III), suggested that the structure of this molecule may be disordered. The final atomic coordinates are shown in Table III.

All calculations were carried out using the GX program package.[18] Neutral-atom scattering factors were taken from ref 19.

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Supplementary Material Available: Tables of anisotropic displacement parameters (SI), bond lengths (SII), and bond angles (SII) (8 pages). Ordering information is given on any current masthead page.

OM920198Z

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[16] Manojlović-Muir, Lj.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* 1974, 2427.

[17] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

[18] Mallinson, P. R.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 51.

[19] *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99, 149.

Reaction Chemistry between CpMo(CO)$_2$(η^3-2-vinylallyl) and Electrophiles: New Carbon–Carbon Bond Formation through Molybdenum η^4-Trimethylenemethane Cationic Intermediates

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The compound CpMo(CO)$_2$(η^3-vinylallyl) (5) underwent a novel cyclization with TCNE and PhCHO (BF_3-catalyzed) in CH_2Cl_2 to afford a six-membered ring product. Treatment of 5 with PhCHO/BF_3·Et_2O in benzene yielded a Mo–η^4-trimethylenemethane salt, generated from the electrophilic addition of PhCHO to the vinyl group of 5. Characterization of this cation has been achieved by IR and ^{1}H NMR spectra and by its subsequent reaction with NaBH$_3$CN and R$_2$CuLi (R = Ph, PhC≡C). Formation of this trimethylenemethane cation is also observed for a similar BF_3-catalyzed reaction between methyl vinyl ketone and acetone in benzene. The synthetic utility of this carbon–carbon-forming reaction in organic synthesis has been investigated and is described.

Introduction

The chemistry of electrophilic addition to the unsaturated hydrocarbon ligand on a neutral metal complex is an important topic in organometallic chemistry.[1-5] This reaction generally leads to the formation of metal-stabilized carbocations. Transition-metal η^1-allyl compounds may represent an instance in which the ligand reacts with H$^+$, Br$^+$, and CH$_3^+$ to give η^2-alkene cations.[6,7] If tetracyanoethylene and p-toluenesulfonyl isocyanate are used as electrophiles, the reaction pathway follows a [3 + 2] cycloaddition pathway.[8,9] Recently, Green et al. reported[10] that a vinyl group adjacent to a π-Mo–allyl moiety could be protonated to give Mo–η^4-*s-trans*-pentadiene cations. Along this direction, we report here the chemistry of

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. P.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 8.

[2] Flood, T. C. In *Topics In Inorganic and Organometallic Stereochemistry*; Geoffroy, G. L., Ed.; Wiley: New York, 1981; Vol. 12, pp 37–117.

[3] Rosenblum, M.; Watkins, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 6316.

[4] Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 493.

[5] Mayr, A.; Shaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1972**, *94*, 6961.

[6] Roseublum, M. *J. Organomet. Chem.* **1986**, *330*, 191 and references therein.

[7] Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31.

[8] Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Organometallics* **1982**, *1*, 1679.

[9] Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585.

[10] Benyunes, S. A.; Green, M.; Grimshire, M. J. *Organometallics* **1989**, *8*, 2268.

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