Carbon−Phosphorus Bond Cleavage in Allyldiphenylphosphine by a Heterobimetallic Ni═Mo Complex and Formation of an Electronically Unsaturated NiMo$_2$ μ-Diphenylphosphido Cluster

Sarah Clapham,[†] Pierre Braunstein,[‡] Neil M. Boag,[†] Richard Welter,[§] and Michael J. Chetcuti*,[△]

University of Salford, Salford, Greater Manchester M5 4WT, England, Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cédex, France, Laboratoire DECOMET, Institut de Chimie (UMR 7177 CNRS), Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cédex, France, and Laboratoire de Chimie Organométallique Appliquée, ECPM (UMR 7509 CNRS), Université Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg, France

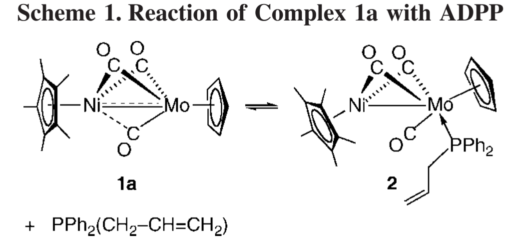
Received September 24, 2007

The unsaturated nickel−molybdenum complex [(η-C$_5$Me$_5$)Ni═Mo(CO)$_3$(η-C$_5$H$_5$)] (*Ni═Mo*), **1**, reacts with allyldiphenylphosphine (ADPP) to give the complex [(η-C$_5$Me$_5$)Ni(μ-CO)$_2$Mo(CO)(κ^1(*P*)-PPh$_2$CH$_2$CH═CH$_2$)(η-C$_5$H$_5$)] (*Ni−Mo*), **2**, which is in equilibrium with the starting materials at ambient temperature. Nevertheless, orange crystals of complex **2** could be isolated from the solution, and a single-crystal X-ray diffraction study confirmed that the phosphine ligand is bound to the molybdenum atom via the phosphorus atom alone. Prolonged heating of complex **1** with excess ADPP led to activation of the P−C$_{allyl}$ bond and to the isolation of the unsaturated trinuclear NiMo$_2$ μ-diphenylphosphido cluster [(η-C$_5$Me$_5$)NiMo$_2$(η-C$_5$H$_5$)$_2$(μ_3-CO)(μ-PPh$_2$)(CO)$_2$], **3**. The structure of this 46-electron cluster was established spectroscopically and by a single-crystal X-ray diffraction study. It is electronically unsaturated and contains a formal Mo═Mo double bond that is spanned by a μ-PPh$_2$ ligand; the molecule exhibits effective mirror plane symmetry in solution, and in the solid state, an approximate mirror plane is also observed.

Introduction

Heterometallic complexes, by their very nature, offer at least two chemically different metallic sites, which are each susceptible to react with various ligands. The concept of metalloselectivity of a reaction then becomes essential.[1,2] The chemistry of heterobimetallic complexes[3] and their ability to carry out hydrocarbyl transformations[4] have led to their being the subject of extensive studies. If one of the metallic centers is coordinatively unsaturated, or potentially so, that metal is likely to be the site of reactivity. Thus, in a series of heterobimetallic complexes with an iron−palladium bond spanned by a hemilabile μ-Si(OMe)$_3$ ligand, the palladium atom can become coordinatively unsaturated, when necessary, by decoordination of the bridging methoxy group.[5] Other examples involve the opening of a metal−metal bond, often of the donor–acceptor type, which leaves one metal center coordinatively unsaturated and thus more reactive.[6,7] The situation is less clear when the unsaturation manifests itself as a metal−metal multiple bond.[8] In this case, both metals can be considered to be potential reactions sites.

Scheme 1. Reaction of Complex 1a with ADPP



Some of our recent research has focused on the coordination chemistry of the complex [Cp*Ni═Mo(CO)$_3$Cp] (*Ni═Mo*) (Cp = η^5-C$_5$H$_5$; Cp′ = η^5-C$_5$H$_4$Me; Cp* = η^5-C$_5$Me$_5$), **1a** (Scheme 1), which can be considered to contain a formal Ni═Mo double bond.[9,10] This heterobimetallic complex contains an oxophilic early transition metal (Mo) bonded to a later group 10 metal (Ni). The chemistry of this unsaturated complex, of its Ni−W

* To whom correspondence should be addressed. E-mail: chetcuti@chimie.u-strasbg.fr.
[†] University of Salford.
[‡] Laboratoire de Chimie de Coordination, Université Louis Pasteur.
[§] Laboratoire DECOMET, Université Louis Pasteur.
[△] Laboratoire de Chimie Organométallique Appliquée, Université Louis Pasteur.

(1) Braunstein, P. In *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; HCA, VCH: Weinheim, Germany, 1992.
(2) Braunstein, P.; Rosé, J. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley VCH: Weinheim (Germany), 1999; Vol. 2.
(3) Chetcuti, M. J. *Compr. Organomet. Chem. II (Rev. Lit. 1982–1994)* **1995**, *9*, 23–84.
(4) Ritleng, V.; Chetcuti, M. J. *Chem. Rev.* **2007**, *107*, 797–858.
(5) Blin, J.; Braunstein, P.; Fischer, J.; Kickelbick, G.; Knorr, M.; Morise, X.; Wirth, T. *J. Chem. Soc., Dalton Trans.* **1999**, *2159*, 2170.
(6) Einstein, F. W. B.; Martin, L. R.; Pomeroy, R. K.; Rushman, P. *J. Chem. Soc., Chem. Commun* **1985**, 345.
(7) Huttner, G.; Schneider, J.; Müller, H.-D.; Mohr, G.; von Seyerl, J.; Wohlfahrt, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 76.
(8) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms 1993*, 2nd ed.; Oxford University Press: Oxford, U.K., 1993.
(9) Chetcuti, M. J.; Grant, P. E.; Fanwick, P. E.; Geselbracht, M. J.; Stacy, A. M. *Organometallics* **1990**, *9*, 1343–1345.
(10) Braunstein, P.; Chetcuti, M. J.; Welter, R. *Chem. Commun.* **2001**, 2508–2509.

10.1021/om700946j CCC: $40.75
Publication on Web 03/18/2008

analogue [Cp*Ni═W(CO)$_3$Cp] (*Ni═W*), **1b**, and of closely related Cp*−nickel-group 6-Cp′ complexes with two electron donor ligands has been, and continues to be, investigated.[11,12] Complex **1b** has been shown to add simple two-electron donor ligands such as di- and trialkylphosphines or an alkyl isocyanide. No structural data were obtained on any of these adducts, though they were fully characterized spectroscopically.[11] However, the data did suggest that two electron donors (small trialkylphosphine ligands, pyridine) coordinate to the group 6 metal. Thus, the ^{31}P NMR spectrum of some of the trialkylphosphine complexes exhibited J_{WP} coupling constants that are typical of one-bond ^{183}W−^{31}P couplings. Many potentially bridging ligands (CO, *t*-BuNC) were found to undergo bridge-terminal exchange: for the *t*-BuNC adducts [Cp*NiW(CO)$_3$(*t*-BuNC)Cp*] (*Ni−W*), isomers with bridging and with terminal *t*-BuNC groups were both observed in the IR spectrum.[11]

A number of previous studies have focused on the reactions of complexes **1** with unsaturated hydrocarbon species such as alkynes and allenes.[13–18] More recently, a study of the reactions of **1** with activated alkenes was initiated. Methylacrylate, CH_2═$CHCO_2Me$, reacted in an unprecedented fashion with **1a** to afford a complex which contained an allylic ligand that resulted from the tail to tail dimerization of two methylacrylate units. The NiMo$_2$ μ_3-carbyne cluster [Mo$_2$NiCp$_2$Cp*(μ_3-CCH$_2$C(O)OMe)(CO)$_4$], which is structurally related to a new cluster described in this work, was also isolated. In both of these reactions, there has been activation of methyl acrylate C−H bonds.[10]

In view of these previous results, the research presented here had two goals. First, we wanted to unambiguously characterize an adduct of **1a** coordinated to a P-donor ligand, by a single-crystal X-ray diffraction study, in order to establish beyond doubt onto which metal the group 15 ligand was bonded to. Second, we believed that the reaction of **1** with a P-donor hemilabile ligand with a pendant olefin functionality might, following initial P-coordination, lead to alkene coordination and/or C−H activation of an olefinic C−H bond.

Allyldiphenylphosphine (ADPP), a bulkier group 15 phosphorus-donor ligand, was the target ligand chosen for this study. This versatile ligand binds to metals in at least three ways: (1) |^1(*P*)- via the phosphorus atom alone,[5,19a–n] (2) in a κ^1(*P*):η^2-mode via both the phosphorus atom and the olefinic *C*═C functionality,[19e,f] or (3) much more rarely, via just the olefinic functionality.[20] Examples of ADPP adopting coordination modes 1 and 2 in the same molecule are also known.[21] Furthermore, this ligand's allylic *C*═C double bond is reactive and has been shown to undergo intramolecular [4 + 2] Diels–Alder cycloaddition reactions with 2*H*-phospholes[22] or intramolecular [2 + 2] cycloaddition with vinylidene *C*═C bonds under mild conditions.[23]

Results and Discussion

I. Reaction of 1a with ADPP To Afford [Cp*Ni(μ-CO)$_2$-Mo(CO)(ADPP)Cp] (*Ni−Mo*) 2. Complex **1a** reacts instantly with ADPP to give a bright orange solution. The color of this solution is temperature dependent and reversibly darkens to a dirty brown color when the solution is heated in hot toluene. This visual observation is consistent with the equilibrium shown in Scheme 1, in which the structure of the product [Cp*Ni(μ-CO)$_2$Mo(CO)(κ^1(*P*)-PPh$_2$CH$_2$CH═CH$_2$)Cp] (*Ni−Mo*), **2**, is shown. Crystals of **2** could be isolated at low temperature (see the Experimental Section). However, NMR studies of solutions of these crystals were not informative as the equilibrium, shown in Scheme 1, shifts to the left. Useful NMR data could not be harvested from the broad featureless spectra observed. The free ADPP and, especially, **1a**, are highly air-sensitive, and **1a** is paramagnetic.[9] The nature of complex **2** was clearly established by means of a single-crystal X-ray diffraction study.

A diagram of complex **2** is shown in Figure 1. Crystal data and data collection parameters and key bond-lengths and angles for **2** are collected in Tables 1 and 2 respectively.

X-ray study of **2** confirms its heterobimetallic nature and establishes the presence of a κ^1(*P*)-PPh$_2$(CH$_2$−CH═CH$_2$) ligand that is coordinated to the molybdenum atom. Two of the carbonyl ligands are now bridging between molybdenum and nickel, as manifested by the short Ni−$C_{\mu\text{-CO}}$ distances of 1.856(7) Å and 1.857(6) Å. These two bridging CO ligands lie in a butterfly geometry with respect to the nickel−molybdenum single bond of 2.6681(9) Å and the two NiMo(μ-C) planes make an angle of 127° with each other. The molybdenum−phosphorus bond is almost perpendicular to the metal−metal vector [Ni−Mo−*P* = 95.56(5)°]. As is observed with most structures to date with a Cp*Ni−MCp (M = Mo, W) group, the two C$_5$ ring centroids are in a *trans*-conformation with respect to each other. The allylic *C*═C bond of the phosphine ligand is not interacting with the metals, but interestingly, the atoms Ni, Mo, P, and C(31), the C$_\alpha$ atom of the allyl group, are essentially in the same plane: the torsion angle made by these four atoms is only 3.4(2)°.

Both nickel and molybdenum ADPP complexes have been isolated. An early classic reference describes the complexes

(11) Chetcuti, M. J.; Deck, K. J.; Fanwick, P. E.; Gordon, J. C.; Grant, B. E. *Organometallics* **1992**, *11*, 2128–2139.
(12) Bartlone, A.; Chetcuti, M. J.; Fanwick, P. E.; Haller, K. A. *Inorg. Chem.* **1993**, *32*, 1435–1441.
(13) Chetcuti, M. J.; McDonald, S. R.; Rath, N. P. *Organometallics* **1989**, *8*, 2077–2079.
(14) Chetcuti, M. J.; Fanwick, P. E.; McDonald, S. R.; Rath, N. N. *Organometallics* **1991**, *10*, 1551–1560.
(15) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1995**, *14*, 2937–2950.
(16) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1996**, *15*, 4389–4397.
(17) Chetcuti, M. J.; McDonald, S. R. *Organometallics* **2002**, *21*, 3162–3168.
(18) Chetcuti, M. J.; McDonald, S. R. *J. Organomet. Chem.* **2004**, *689*, 1882–1889.
(19) (a) Browning, M. C.; Mellor, J. R.; Morgan, D. J.; Pratt, S. A. J.; Sutton, L. E.; Venanzi, L. M. *J. Chem. Soc.* **1961**, *693*, 703. (b) Gul, N.; Nelson, J. H. *Organometallics* **2000**, *91*, 104. (c) Coles, S. J.; Faulds, P.; Hursthouse, M. B.; Kelly, D. G.; Ranger, G. C.; Toner, A. J.; Walker, N. M. *J. Organomet. Chem.* **1999**, *586*, 234–240. (d) Ershova, V. A.; Golovin, A. V.; Sheludyakova, L. A.; Semyannikov, P. P.; Pomogailo, S. I.; Pomogailo, A. D. *Russ. Chem. Bull.* **2000**, *49*, 1448–1453. (e) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171–185. (f) Díez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Villar, A. *Eur. J. Inorg. Chem.* **2006**, 78–87. (g) Baker, P. K.; Flower, K. R. *Polyhedron* **1990**, *9*, 2233–2237. (h) Baker, P. K.; Flower, K. R. *J. Organomet. Chem.* **1991**, *405*, 299–307. (i) Jegorov, A.; Turecek, F. *J. Organomet. Chem.* **1989**, *379*, C5–C6. (j) Treichel, P. M.; Wong, W. K. *Inorg. Chim. Acta* **1979**, *33*, 171–175. (k) Wang, I. H.; Wermer, P. H.; Dobson, C. B.; Dobson, G. R. *Inorg. Chim. Acta* **1991**, *183*, 31–38. (l) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639–2645. (m) Coles, S. J.; Faulds, P.; Hursthouse, M. B.; Kelly, D. G.; Ranger, G. C.; Walker, N. M. *J. Chem. Res., Synop.* **1999**, *7*, 418–419, and 1811–1824. (n) Que, L.; H, P. L. *Inorg. Chem.* **1973**, *12*, 156.
(20) Pomogailo, S. I.; Chuev, I. I.; Dzhardimalieva, G. I.; Yarmolenko, A. V.; Makhaev, V. D.; Aldoshin, S. M.; Pomogailo, A. D. *Russ. Chem. Bull.* **1999**, *48*, 1174–1177.
(21) Barthel-Rosa, L. P.; Maitra, K.; Nelson, J. H. *Inorg. Chem.* **1998**, *37*, 633–639.
(22) Maitra, K.; Catalano, V. J.; Nelson, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 12560–12567.
(23) Alvarez, P.; Lastra, E.; Gimeno, J.; Bassetti, M.; Falvello, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 2386–2387.

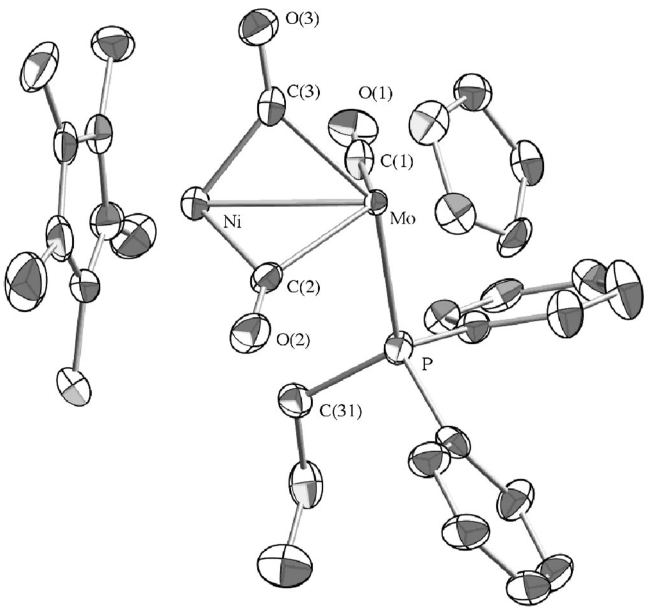


Figure 1. Thermal ellipsoid plot at the 50% probability level of all non-hydrogen atoms of [(η-C_5Me_5)Ni(μ-CO)$_2$Mo(CO)(κ^1(*P*)-($PPh_2CH_2CH{=}CH_2$)(η-C_5H_5)] (*Ni*−*Mo*), **2**. Key atoms are labeled.

Table 1. Crystal Data and Structure Refinement for Complexes [(η-C_5Me_5)Ni(μ-CO)$_2$Mo(CO)(κ^1(*P*)-PPh_2CH_2−CH=CH_2)(η-C_5H_5)] (*Ni*−*Mo*) 2 and [$NiMo_2$(μ_3-CO)(μ-PPh_2)(CO)$_2$(η-C_5Me_5)(η-C_5H_5)$_2$], 3, with Estimated Standard Deviations in Parentheses

complex	2	3
empirical formula	$C_{33}H_{35}MoNiO_3P$	$C_{35}H_{35}Mo_2NiO_3P$
mol wt	665.23	785.19
T, K	173(2)	173(2)
wavelength, Mo Kα, Å	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	*P*2$_1$/*c*	*C*2/c
unit cell dimens, Å		
a	9.2377(3)	42.922(5)
b	31.9049(9)	14.0273(10)
c	9.9119(3)	10.2398(10)
α, deg	90	90
β, deg	92.24(2)	92.03(5)
<γ, deg	90	90
V, Å^3	2919.08(15)	6161.3(10)
Z	4	8
calcd density, g cm^{-3}	1.514	1.693
abs coeff, mm^{-1}	1.162	1.493
F(000)	1368	3168
cryst size, mm	0.08 × 0.07 × 0.05	0.1 × 0.1 × 0.1
θ range for data collecn, deg	2.15−27.52	2.03−30.02
index ranges	$-11 \le h \le 11$	$-60 \le h \le 60$
	$-38 \le k \le 41$	$0 \le k \le 19$
	$-12 \le l \le 12$	$0 \le l \le 14$
no. of rflns collected	10982	8995
no. of indep rflns	6666	8995
no. of variables	352	374
final *R*index ($I > 2\sigma(I)$)	0.0881, wR = 0.1253	0.0394, wR = 0.0909
*R*index (all data)	0.1734, wR = 0.1558	0.0593, wR = 0.0975

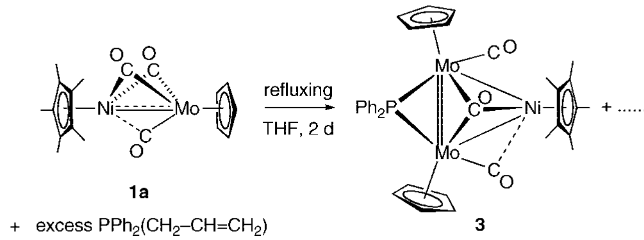
[NiX_2(ADPP)$_2$] (X = Cl, Br, I) and the delicately balanced choice of structures (tetrahedral or square planar), depending on the nature of X.[19a] However, while molybdenum and other group 6 metal complexes[19g,h,j,k,22,24] with phosphorus bound ADPP ligands have been described, neither these, nor any of the nickel complexes,[19a,m,n] appear to have been structurally characterized.

Table 2. Key Bond Distances (Å), Bond Angles, and Torsion Angles (deg) of [(η-C_5Me_5)Ni(μ-CO)$_2$Mo(CO)(κ^1(*P*)-PPh_2CH_2−CH=CH_2)(η-C_5H_5)] (*Ni*−*Mo*) 2, with esd's in Parentheses

Mo−Ni	2.6681(9)	Mo−C(1)	1.969(7)
Mo−C(2)	2.154(7)	Mo−C(3)	2.101(7)
Mo−P	2.5135(18)	Ni−C(2)	1.857(6)
Ni−C(3)	1.856(7)	P−C(19)	1.843(6)
C(19)−C(20)	1.498(9)	C(20)−C(21)	1.304(11)
Mo−C_{cp}	2.32(6)	Ni−C_{Cp*}	2.16(5)
Mo-Cp_{cent}	1.982	Ni-Cp_{cent}	1.780
Mo−C(1)−O(1)	175.0(6)	Mo−C(2)−O(2)	143.0(5)
Mo−C(3)−O(3)	141.9(5)	Ni−C(3)−O(3)	133.5(5)
Ni−C(2)−O(2)	133.7(5)	Ni−Mo−P	95.6(1)
Ni−Mo−C(1)	79.5(2)	Mo−P−C_{all}	115.6(2)
Cp^*_{cent}−Ni−Mo	161.9	Cp_{cent}−Mo−Ni	144.2
Ni−Mo−P−C_{all}	3.4(2)	Cp^*_{cent}−Ni−Mo−Cp_{cent}	153.5

dihedral angle between Ni−C(2)−Mo and Ni−C(3)−Mo planes: 126.7°

Scheme 2. Formation and Structure of Complex 3



II. Further Reaction of ADPP with 1a to Give the $NiMo_2$ μ-Diphenylphosphido Cluster [Cp*$NiMo_2Cp_2$(μ_3-CO)(μ-PPh_2)(CO)$_2$], 3. The structure of complex **2** clearly showed that the allylic double bond of the ADPP ligand was not interacting with the dimetallic moiety. Conversion of κ^1(*P*)-coordinated ADPP ligands to an κ^1:η^2(*P*, *C*=C)-coordination mode is known and, in carbonyl complexes, may be induced by thermal or photochemical loss of CO ligands.[19k] Thus, in an attempt to induce coordination of this olefin double bond to one of the metals, a solution of **1a** and 1 molar equiv of ADPP was refluxed for 2 days in THF. The initial orange color of the *in situ* solution of **2** gave way to a dark brown color. After workup and chromatography on an alumina column (see the Experimental Section) a dark green solution, which contained complex **3**, was eluted. Dark green crystals of **3** were isolated from this solution. The dark color of **3** hinted at its nature as a polymetallic species. Longer reflux period (4 days) led to extensive decomposition and no traces of **3** could be isolated under these more forcing reaction conditions. The thermolysis reaction was repeated using a 5-fold excess of ADPP, but the isolated yield of **3** did not change significantly. The reaction was attempted photochemically, but massive decomposition ensued and complex **3** could not be isolated. Addition of a 0.5 molar equiv of [Mo(CO)$_3$Cp]$_2$ (Mo−Mo) had no effect on the photochemical reaction. Furthermore, the yields of **3** were not increased by adding 0.5 molar equiv of the molybdenum dimer. However, the triply bonded [Mo(CO)$_2$Cp]$_2$ (Mo≡Mo) was also recovered under these conditions.

The ^{1}H NMR data for **3** were surprisingly simple. Only three sets of signals were observed at chemical shifts that were characteristic of Ph proton multiplets and of Cp and Cp* proton singlets. The integral ratios of the Ph multiplets and the Cp and Cp* singlets indicated that these groups were present, respec-

(24) Maitra, K.; Wilson, W. L.; Jemin, M. M.; Yeung, C.; Rader, W. S.; Redwine, K. D.; Striplin, D. P.; Catalano, V. J.; Nelson, J. H. *Syn. React. Inorg. Met.-Org. Chem.* **1996**, *26*, 967.

Table 3. Key Bond Distances (Å) and Bond and Torsion Angles (deg) of the Cluster [$NiMo_2$(μ_3-CO)(μ-PPh_2)$(CO)_2$(η-C_5Me_5)(η-C_5H_5)$_2$],3 with esd's in Parentheses

Mo(1)−Ni	2.6420(12)	Mo(2)−Ni	2.6662(5)
Mo(1)−C(1)	1.983(3)	Mo(2)−C(2)	1.981(3)
Mo(1)−C(3)	2.158(3)	Mo(2)−C(3)	2.203(3)
Mo(1)−P	2.3767(10)	Mo(2)−P	2.3684(11)
Ni···C(1)	2.469(3)	Ni−C(3)	1.888(3)
Mo(1)−Mo(2)	2.6857(8)		
Ni−C_{Cp*}	2.14(2)	Ni−Cp_{cent}	1.759
Mo(1)−C_{Cp}	2.30(2)	Mo(1)−Cp(1)$_{cent}$	1.996
Mo(2)−C_{Cp}	2.33(1)	Mo(2)−Cp(2)$_{cent}$	2.003
Ni−Mo(1)−Mo(2)	60.1(2)	Ni−Mo(2)−Mo(1)	59.2(1)
Mo(1)−Ni−Mo(2)	60.8(1)	Mo(1)−P−Mo(1)	68.9(1)
Mo(2)−Mo(1)−P	55.4 (1)	Mo(1)−Mo(2)−P	55.7 (1)
Ni−Mo(1)−P	111.1(1)	Ni−Mo(2)−P	110.5(1)
Mo(1)−C(1)−O(1)	166.8(2)	Mo(2)−C(2)−O(2)	172.3(3)
Mo(1)−C(3)−O(3)	134.8(2)	Mo(2)−C(3)−O(3)	132.4(2)
Ni−C(3)−O(3)	130.3(2)	C(1)−Mo(1)−Mo(2)− C(2)	6.1(1)
Cp(1)$_{cen}$−Mo(1)−Mo(2)−Cp(2)$_{cen}$	4.8		
dihedral angle between Ni−Mo(1)−Mo(2) and P−Mo(1)-Mo(2) planes:	154.5°		
Dihedral angle between C(3)−Mo(1)−Mo(2) and P−Mo(1)−Mo(2) planes:	151.5°		

tively, in a 2:2:1 ratio. Surprisingly, no allylic proton resonances were observed. The presence of phosphorus was confirmed by the single resonance observed in the ^{31}P NMR spectrum of **3**, with a chemical shift of δ = 165 ppm typical of bridging phosphido ligands. The IR spectrum of complex **3** showed absorption bands that could be attributed to both terminal and bridging CO ligands. Collectively, these spectroscopic data did not allow the unambiguous determination of the structure, and a single crystal X-ray structural analysis was performed. This study established the formulation of complex **3** as [$Cp^*NiMo_2Cp_2$(μ_3-CO)(μ-PPh_2)$(CO)_2$]. Scheme 2 shows the synthesis and structure of **3**.

Crystal and data collection parameters for complex **3** are collected in Table 1. Selected bond lengths and angles are listed in Table 3. A plot of **3** showing all non-hydrogen atoms is shown in Figure 2.

This heterotrinuclear cluster consists of a $NiMo_2$ triangle with a triply bridging CO group capping the three metals. The two molybdenum atoms are symmetrically bridged by a μ-PPh_2 ligand [Mo(1)−P = 2.3767(10) Å; Mo(2)−P = 2.3684(11) Å]. In accord with the spectroscopic data, the allylic group is completely absent from the molecule.

The Mo−Mo distance of 2.6857(8) Å in the cluster is short, too short to be a single bond. Internuclear Mo−Mo bonds are highly variable and are often a function of the number and type of bridging ligands present and not just of the bond order. The assignment of bond order based solely on the molybdenum−molybdenum distance is thus risky, especially with bridging ligands. Nevertheless, the molybdenum−molybdenum distance in **3**, together with the fact that **3** is a 46-electron cluster, suggest that a Mo═Mo double bond is indeed present. Cluster **3** is closely related to other clusters with Mo_2M (M = Cr, Mo, W, Mn) cores that have been recently described that also contain localized Mo═Mo bonds spanned by μ-PR_2 ligands.[25,26]

In structurally characterized bimetallic complexes or clusters, with localized Mo═Mo double bonds, these distances are typically less than 2.80 Å (see Table 4).[25–27] Most Mo−Mo single bonds are longer and are usually found in the 2.80–3.20 Å range (see a few examples in Table 5),[10,27d,28–30] though much longer Mo−Mo distances of up to 3.453(2) Å have been observed.[31] For comparison, the Mo−Mo distance in the dinuclear complex [$CpMo(CO)_2$]$_2$ which contains a metal−metal triple bond is 2.448(1) Å.[32]

(25) Alvarez, C. M.; Alvarez, M. A.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **2005**, *24*, 7.

(26) Alvarez, C. M.; Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A.; Graiff, C.; Tiripicchio, A. *Organometallics* **2007**, *26*, 321–331.

(27) (a) Chisholm, M. H.; Kelly, R. L.; Cotton, F. A.; Extine, M. W. *J. Am. Chem. Soc.* **1978**, *100*, 2256–2257. (b) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645–7650. (c) Herrmann, W. A.; Bell, L. K.; Ziegler, M. L.; Pfisterer, H.; Pahl, C. *J. Organomet. Chem.* **1983**, *247*, 39–60. (d) Gibson, C. P.; Rae, A. D.; Tomchick, D. R.; Dahl, L. F. *J. Organomet. Chem.* **1988**, *340*, C23-C30. (e) King, H. E. J.; Mundi, L. A.; Strohmaier, K. G.; Haushalter, R. C. *J. Solid State Chem.* **1991**, *92*, 1–7. (f) Saadeh, C.; Colbran, S. B.; Craig, D. C.; Rae, A. D. *Organometallics* **1993**, *12*, 133–139. (g) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, *1555*, 1564. (h) Benson, I. B.; Killops, S. D.; Knox, S. A. R.; Welch, A. J. *J. Chem. Soc., Chem. Commun* **1980**, 1137. (i) Budzichowski, T. A.; Chisholm, M. H.; Folting, K.; Kramer, K. S. *Polyhedron* **1996**, *15*, 3085–3091. (j) Kuhn, N.; Zauder, E.; Boese, R.; Blaeser, D. *Inorg. Chem.* **1988**, *8*, 2171–2175. (k) Poder-Guillou, S.; Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W.; Baguley, P. *Inorg. Chim. Acta* **1997**, *257*, 153–161.

(28) Curtis, M. D.; Williams, P. D.; Butler, W. M. *Inorg. Chem.* **1988**, *27*, 2853–2862.

(29) Schollhammer, P.; Pétillon, F. Y.; Pichon, R.; Poder-Guillou, S.; Talarmin, J.; Muir, K. W.; Manojlovic-Muir, L. *Organometallics* **1995**, *14*, 2277–2287.

(30) Shaposhnikova, A. D.; Drab, M. V.; Kamalov, G. L.; Pasynskii, A. A.; Eremenko, I. L.; Nefedov, S. E.; Struchkov, Y. T.; Yanovsky, A. I. *J. Organomet. Chem.* **1992**, *429*, 109–118.

(31) Wang, B.; Zhu, B.; Xu, S.; Zhou, X. *Organometallics* **2003**, *22*, 2842–2852.

(32) Klinger, R. J.; Butler, N. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034.

(33) (a) Azar, M. C.; Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 7209–7210. (b) Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298–2306. (c) Chetcuti, M. J.; DeLiberato, L.; Fanwick, P. E.; Grant, B. E. *Inorg. Chem.* **1990**, *29*, 1295–1298. (d) Nakajima, T.; Mise, T.; Shimizu, I.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5598–5604. (e) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.-Y.; Naceur, J. B.; Mentzen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123–1130. (f) Chetcuti, M. J.; McDonald, S. R.; Huffman, J. C. *Inorg. Chem.* **1989**, *28*, 238–242. (g) Braunstein, P.; Chetcuti, M. J.; Welter, R. *C. R. Chim.* **2002**, *5*, 67–72. (h) Curtis, M. D.; Ping, L. *J. Am. Chem. Soc.* **1989**, *111*, 8279–8280. (i) Bian, Z.-G.; Zhang, W.-Q.; Guan, H.-X.; Yin, Y.-Q.; Q.-S., L.; Sun, J. *J. Organomet. Chem.* **2002**, *664*, 201–207. (j) Song, L.-C.; Dong, Y.-B.; Hu, Q.-M.; Wu, B.-M.; Mak, T. C. W. *Chin. J. Struct. Chem.* **1995**, *14*, 393. (k) Song, L. C.; Dong, Y. B.; Hu, Q. M.; Huang, X. Y.; Sun, J. *Organometallics* **1997**, *16*, 4540.

(34) Pomogailo, S. I.; Shilov, G. V.; Ershova, V. A.; Virovets, A. V.; Pogrebnyak, V. M.; Podberezskaya, N. V.; Golovin, A. V.; Dzhardimalieva, G. I.; Pomogailo, A. D. *J. Organomet. Chem.* **2005**, *690*, 4258–4264.

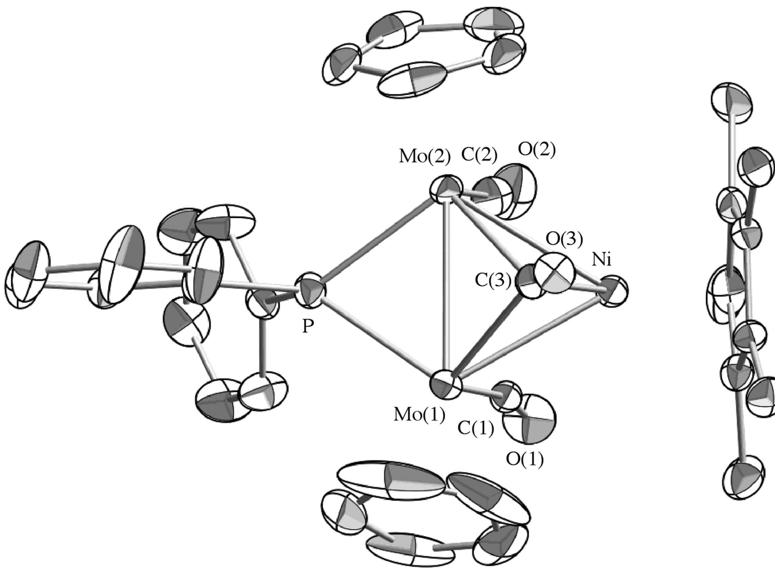


Figure 2. Thermal ellipsoid plot at the 50% probability level of all non-hydrogen atoms of [(η-C_5Me_5)NiMo_2(η-C_5H_5)$_2$(μ_3-CO)(μ-PPh_2)$(CO)_2$], **3**. Key atoms are labeled.

Table 4. Molybdenum−Molybdenum Distances Found in Bimetallic Complexes and Clusters Both with Formal Mo=Mo Bonds

complex	Mo=Mo distance (Å)
[$Mo_3(CO)_4(\mu_3$-CO)(μ-PCy_2)Cp_3][25]	2.743(1)
[$Mo_2WCp_2(\mu_3$-H)(μ-PCy_2)$(CO)_7$][26]	2.6351(5)
[$MnMo_2Cp_2Cp'(\mu_3$-H)(μ-PCy_2)$(CO)_4$][26]	2.6448(8)
[Mo_2(O-*t*-Bu)$_4$(μ-O-*t*-Bu)$_2$(μ-CO)][27a,b]	2.498(1)
[Cp*Mo(CO)(N=C=O)(μ-η^1-N=CMe_2)Mo$(CO)_2$Cp*][27c]	2.745(2)
[$Mo_3(CO)_4(\mu_2$-H)(μ_3-O)Cp^*_3][27d]	2.660(1)
[$NH_4Mo_2P_2O_{10}$]·H_2O[27e]	2.453(2)
[$Mo_2(\mu$-Br)$_2$(μ-CO)$_2$(η^5-$C_5Ph_4Ar)_2$ [Ar = $C_6H_3(OMe)_2$-2,5][27f]	2.641(2)
[$Mo_2(\mu$-$PPh_2)_2(CO)_2Cp_2$][27g]	2.712(2)
[$Mo_2(\mu$-S-*t*-Bu)$_2(CO)_2Cp_2$][27h]	2.616(2)
[$Mo_2(PMe_3)_4(\mu$-O)(μ-OCH_2-*t*-Bu)(OCH_2-*t*-Bu)$_3$][27i]	2.4931(9)
[Cp(CO)Mo(μ-$SMe_2)_2$Mo(PMe_3)Cp][$BF_4]_2$[27j]	2.693(1)
[$Mo_2(\mu$-Br)(μ-O)(μ-SMe)$Br_2Cp^*_2$][27k]	2.755(1)

Table 5. Molybdenum−Molybdenum Distances in a Few Bimetallic Molecules or Clusters with Formal Mo−Mo Single Bonds

complex	Mo−Mo distance (Å)
[$Mo_2(CO)_6Cp_2$][37]	3.235(1)
[$Mo_2Ni(\mu_3$-CCH_2C(O)OMe)$(CO)_4Cp_2Cp^*$][10]	2.9343(4)
[$Mo_3(CO)_4(\mu_2$-H)(μ_3-O)Cp^*_3][27d]	2.916(1), 2.917(1)
[$Mo_2Ni_2(CO)_2(\mu_3$-S)$_4Cp'_2$][28]	2.829(1)
[$Mo_2(CO)_2(\mu$-SMe)$_2$(μ-SH)$Cp^*_2]^+$ [29]	2.772(2)
[$Mo_4(\mu_3$-OH)(μ_3-CPh)$_2$(μ_6-C)$Co_3(\mu$-CO)$_3(CO)_3Cp_4$][30]	2.761(4)−2.939(4)
[$Mo_3(CO)_4(\mu_3$-CO)(μ-PCy_2)Cp_3][25]	3.085(1), 3.094(1)

In contrast to the Mo=Mo bond present, the marginally different Ni−Mo distances of 2.6420(4) and 2.6662(5) Å in **3** are unremarkable and are typical of Ni−Mo single bonds observed in such dimetallic compounds and in related metal clusters (see Table 6).[10,13,14,30,33]

If one neglects the slight twist of the phenyl groups, and of the C_5H_5 groups relative to each other (that destroy the mirror plane), the molecule contains an approximate mirror plane that bisects the Mo=Mo bond and passes through the nickel atom. Each molybdenum atom is bonded to a carbonyl ligand, and these ligands approximately eclipse each other. One of these CO ligands interacts slightly with the nickel atom in a semibridging fashion [Mo−C(1)−O(1) = 166.8(2)°, Ni···C(1) = 2.468 Å, while the other CO ligand is best considered to be terminal, with insignificant Ni−C interactions [Mo−C(2)−O(2) = 172.3(3)°, Ni···C(2) = 2.704 Å].

Table 6. Molybdenum−Nickel Distances in Representative Compounds

complex	Ni−Mo distance (Å)
[$Mo_2Ni(\mu_3$-CCH_2C(O)OMe)$(CO)_4Cp_2Cp^*$][10]	2.6282(5), 2.6309(5)
[Cp′Mo$(CO)_2$(μ-η^1, η^3-CMe-CMe-CH_2)NiCp][13,14]	2.577(2)
[$Mo_2Ni_2(CO)_2(\mu_3$-S)$_4Cp'_2$][28]	2.720(1), 2.723(1)
[$Ni_2Mo_2(\mu_3$-CPh)$_2(\mu_3$-CO)$_2Cp_4$][30]	2.664(2)
Cp′Mo$(CO)_2$(μ-η^2, η^2-C(Me)C(Me)C(O))NiCp][33a,b]	2.5859(2)
[CpMo$(CO)_2$(μ-η^2,η^4-CHCPhCPhCH)Ni(μ-PhC_2H)-NiCp*][33c]	2.6731(4)
[Cp_2MoH(μ-CO)NiCp*][33d]	2.657(1)
[FeMoNi$(CO)_4$($PhC_2CO_2{}^iPr$)Cp_2][33e]	2.616(2)
[$MoNi_3(\mu_3$-CO)$_3Cp_3Cp'$][33f]	2.590(2), 2.594(2), 2.597(2)
[FeMoNi(μ_3-CO)(μ_2-CO)$(CO)_3$CpCp*][33g]	2.658(2), 2.659(2)
[$Mo_2Ni_2(\mu_3$-S)$_2(\mu_4$-CO)Cp_4][33h]	2.680(1)
[MoNiRu$(CO)_5(\mu_3$-S)Cp(η^5-C_5H_4COMe)][33i]	2.6479(7)
[MoNiRu$(CO)_5(\mu_3$-S)Cp(η^5-C_5H_4C(NR)Me)],[33i] R = 2,4-$C_6H_3(NO_2)_2$]	2.7261(14)
[FeMoNiS$(CO)_5$Cp(η^5-$MeCOC_5H_4$)][33j,k]	2.652(1)
[FeMoNiS$(CO)_5]_2$Cp[η^5-$C_5H_4C(O)CH_2]_2$[33k]	2.639(2)

The geometry of the $NiMo_2$ cluster **3** is quite different from that of a $NiMo_2$ alkylidyne cluster [$Mo_2NiCp_2Cp^*(\mu_3$-CCH_2C(O)OMe)$(CO)_4$] whose structure we have recently reported.[10] This alkylidyne cluster has C_1 symmetry, which renders the two molybdenum atoms and their associated ligands inequivalent in both the solid state and, by spectroscopy, in solution. In addition, the latter alkylidyne cluster contains a single Mo−Mo bond, as opposed to the formal Mo=Mo double bond observed in cluster **3**. However, the structure of **3** is closely related to that of some recently reported trinuclear clusters, which also contain localized Mo=Mo bonds.[25,26]

In complex **3** the P−$C_{(allyl)}$ bond in the ADPP ligand has been broken. Phosphorus−carbon bond cleavage reactions are not unknown and are a factor in the deactivation of metal-phosphine complexes in catalytic reactions.[19e] However, rupture of the

P−C bond in ADPP is somewhat unusual since this bond has been shown to be thermally stable when ligated onto an Os_3 hydrido framework and heated.[19d] Indeed, the ADPP in these Os_3 clusters has been copolymerized with styrene.[34] It is interesting and probably relevant to note that in the molecular structure of complex **2**, the Ni, Mo, P and the α-carbon atoms of the allyl group are essentially coplanar [the Ni−Mo−P−C_{all} torsion angle = 3.43°]. A molecular vibration that causes Mo−P−C bending, possibly coupled with a Ni−Mo−P bend, would make the P−C_{allyl} bond approach and interact closely with the nickel atom. The P−C activation reaction that leads to complex **3** may be the result of this interaction and subsequent bond scission.

The reaction of **1b** with PPh_2H has already been reported, and interestingly, complex **3** was not obtained in this reaction.[11] Initial coordination of the secondary phosphine to the tungsten atom gave the Ni−W PPh_2H analogue of complex **2**, namely the species [Cp*Ni(μ-CO)$_2$W(CO)(PPh$_2$H)Cp] (*Ni−W*)]. Oxidative addition of the Ph_2P−H bond then took place to give the phosphido−hydride complex of presumed structure [Cp*Ni(μ-PPh$_2$)(μ-H)W(CO)$_2$Cp].

Reactions of group 15 two-electron donor ligands with the unsaturated complex **1** are complicated as the products are commonly in equilibrium with **1** and the free ligand. In addition, while in most cases coordination to the group 6 metal is observed, there is evidence that with amines, Ni-coordination of the group 15 donor atom takes place. Based on previously obtained spectroscopic data and isolated products, and as shown with the structural determination of **2** reported in this paper, the thermodynamically stable coordination site for complexes **1** with trialkyl- and triarylphosphine ligands is the group 6 metal. We have previously reported that the reaction of CpNi(PMe$_3$)Cl with [W(CO)$_3$Cp]$^-$ results in a PMe_3 migration and affords the complex CpNi(CO)-W(CO)$_2$(PMe$_3$)Cp. This again indicates a greater thermodynamic stability for a group-6 metal bound trialkylphosphine ligand.[11]

Conclusion

When the unsaturated 32 electron complex [Cp*Ni═Mo(CO)$_3$Cp], **1a**, was reacted with ADPP, the molybdenum-bound ADPP complex [Cp*Ni(μ-CO)$_2$Mo(CO)(l^1(*P*)-ADPP)Cp] (*Ni−Mo*), **2**, was isolated. The dinuclear complex **2** is in equilibrium in solution with the free ligand and **1a**. A single crystal X-ray diffraction study of **2** confirmed that the group 15 ligand was bound to the molybdenum atom. When an in situ solution of **2** and excess free ADPP was heated in solution, P−C_{allyl} bond cleavage occurred and the unsaturated cluster [Cp*NiMo$_2$Cp$_2$(μ_3-CO)(μ-PPh$_2$)(CO)$_2$] **3** with a localized Mo═Mo double bond was isolated. The Mo═Mo bond is spanned by a μ-PPh$_2$ ligand derived from the P−C_{allyl} bond cleavage reaction.

Experimental Section

All manipulations were undertaken under an inert atmosphere of purified nitrogen or argon using standard Schlenk tube and vacuum line procedures. Diethyl ether, THF, 1,2-dimethoxymethane (DME), pentane, and hexanes were distilled over sodium benzophenone ketyl; toluene was distilled over sodium and dichloromethane over CaH_2. Complex **1** was prepared according to the published procedure.[33g] ADPP (Aldrich) was used as received. IR spectra were recorded on a Perkin-Elmer 1600 FT-spectrometer using KBr cells. NMR spectra were obtained on a Bruker AC-300 instrument, at room temperature, and chemical shifts are recorded relative to an internal TMS standard (^{1}H NMR) or to an external reference of H_3PO_4 (^{31}P{^{1}H} NMR).

Reaction of Complex 1 with ADPP To Afford [Cp*Ni(μ-CO)$_2$MoCp(CO)(κ^1(*P*)-PPh$_2$CH$_2$CH═CH$_2$)] (*Ni−Mo*), 2. Complex **1a** (0.338 g, 0.77 mmol) was dissolved in THF (20 mL), and ADPP (173 μL, 0.80 mmol) was introduced, dropwise, via microsyringe. An immediate color change from blue-green to orange-brown was observed. The solution was stirred at ambient temperature for 30 min and the volume of THF was then reduced to ca. 2 mL. Recrystallization at –20 °C by slow diffusion of degassed pentane into the THF solution afforded orange crystals of **2** (0.104 g, 0.16 mmol, 20%) that were suitable for single crystal X-ray analysis. This product could not be well characterized in solution by NMR spectroscopy owing to a reversible equilibrium between **2** and the starting materials **1a** and PPh$_2$(CH$_2$−CH═CH$_2$). Anal. Calcd for $C_{33}H_{35}MoNiO_3P$ (665.24): C, 59.58; H, 5.30. Found: C, 59.70; H, 5.26. MS (*m/e*, AMU): 666 (M$^+$), 440 (M − ADPP)$^+$.

Reaction of Complex 1a with ADPP to Afford the Heterotrinuclear Cluster [Cp*NiMo$_2$Cp$_2$(μ_3-CO)(μ-PPh$_2$)(CO)$_2$], 3. Complex **1** (0.438 g, 1.00 mmol) was dissolved in toluene (50 mL) to give a blue-green solution. Dropwise addition of ADPP (1.22 mL, 1.02 mmol) led to an immediate color change to orange-brown. The solution was heated to 90 °C for 48 h during which time it turned dark brown. The solution was then concentrated in vacuo to a volume of ca. 5 mL and subjected to chromatography on an alumina column, using toluene as the initial eluent, followed by increasing percentages of dichloromethane. Six distinct bands were eluted (in order of elution, there were two red bands, an orange band, and two orange brown bands, and finally a dark green band). The first five products were present in tiny quantities and could not be characterized. However, the sixth band was collected and the solvent was removed in vacuo. The dark colored solid formed was dissolved in dichloromethane and crystallized by slow diffusion of pentane at –20 °C. Dark green black crystals of **3** (0.164 g, 0.21 mmol, 21%) deposited. The reaction was also carried out using a 5-fold excess of ADPP but the yield of the cluster **3** was not significantly different.

IR [ν(CO), CH$_2$Cl$_2$]: 1925 (br s), 1769 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): 6.86–7.73 (m, 10H, Ph), 4.88 (s, 10H, C$_5$H$_5$), 1.77 (s, 15H, C$_5$Me$_5$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 164.8 ppm. Anal. Calcd for $C_{35}H_{35}Mo_2NiO_3P$ (785.2): C, 53.54; H, 4.49. Found: C, 53.65; H, 4.57.

X-ray Diffraction Studies. A single crystal of **2** suitable for an X-ray diffraction study was selected from a batch of crystals obtained from a THF solution of **2** at −25 °C. Crystals of complex **3** were harvested from a mixed THF/pentane solvent system at −25 °C. Diffraction data for both crystals were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A summary of crystal data, data collection parameters, and structure refinements are given in Table 1. Cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in φ angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software. Absorption corrections were not applied. All nonhydrogen atoms were refined anisotropically in both structures. One of the Cp rings in complex **3** exhibits somewhat large thermal ellipsoids, indicating some rotational disorder may be present. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.[35,36]

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as

(35) Kappa CCD Operation Manual: Delft, The Netherlands, 1997.
(36) Sheldrick, G. M. SHELXL97, Program for the refinement of crystal structures; University of Gottingen: Germany, 1997.
(37) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086–1090.

supplementary publication nos. CCDC 648714 and 648715. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223–336–033; e-mail: deposit@ccdc.cam.ac.uk; www:http://www.ccdc.cam.ac.uk).

Acknowledgment. We thank the Ministère de la Recherche and the CNRS for grants to M.J.C. while in the LCC and the Université Louis Pasteur and the Région Alsace for financial support. M.J.C. also thanks Pierre Braunstein for his warm welcome and hospitality during his extended stay in Dr. Braunstein's laboratory where most of this research was conducted. S.C. is grateful for an Erasmus mobility grant which allowed her to spend 6 months in Strasbourg.

Supporting Information Available: CIF files of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700946J