positional parameters for non-hydrogen atoms are given in Table II.

A drawing of the structure showing the labeling scheme is given in Figure 1. Bond distances and angles are reported in Table III. The structure consists of monomeric units of $[Pd(Tsgly\text{-}N,O)_2]^{2-}$ anions and sodium ions. The Pd atom shows a square-planar trans coordination given by two centrosymmetrically related Tsgly-*N,O* dianions acting as bidentate ligands through one carboxylate oxygen and the deprotonated sulfonamide nitrogen. The four atoms of the chelating group N–C(2)–C(1)–O(1) show deviations from their mean plane ranging from –0.0886 to 0.0876 Å, with the Pd atom –0.2780 Å out of this plane. The PdN_2O_2 coordination plane forms an angle of 10.39° with the former plane. The Pd–N bond is slightly longer as compared to the average values observed in *cis*-bis(amino acidato)palladium systems[9–12] (2.042 vs 2.02 Å), while the Pd–O bond is slightly shorter by a comparable amount (1.979 vs 2.013 Å).

The Pd is involved in intramolecular contacts with the S, O(4), and C(8) atoms of the two centrosymmetrically related tosyl groups (Pd–S = 3.29 (1), Pd–O(4) = 3.44 (1), Pd–C(8) = 3.83 (1) Å) and shows an intermolecular contact with $C(9)^i$ (i represents the equivalent position $x, y, z + 1$) ($Pd\text{–}C(9)^i$ = 3.99 (1) Å).

In the ligand molecule the S–N and S–C bond distances fall in the range observed for other structurally known copper(II) complexes with the Tsgly-*N,O* dianion.[3,13] The Na^+ ion exhibits a distorted octahedral geometry due to six oxygen atoms and is the main factor responsible for the crystal packing.

The infrared data (the band maximum positions are reported as supplementary material) for the $Na_2[Pd(Tsgly\text{-}N,O)_2]$ species show the usual features of copper(II) complexes with N-deprotonated tosylated amino acidate ligands.[3,14] The band positions for the (phenylsulfonyl)glycine derivative are very similar to those of the former species. This is indicative of the presence of a N-deprotonated ligand molecule involved in metal coordination. In addition, the split of the bands attributed to the carboxylate and sulfonic groups suggests that the environment of the two ligand molecules is somewhat different.

Acknowledgment. We are grateful to the Centro Interdipartimentale Grandi Strumenti (CIGS) of the University of Modena, which supplied the diffractometer and the FT-IR spectrophotometer, the Centro Interdipartimentale di Calcolo Elettronico of the University of Modena for computing support, and the Ministero dell'Università e Ricerca Scientifica for financial support.

Registry No. $Na_2[Pd(Tsgly\text{-}N,O)_2]$, 125303-16-4; $Na_2[Pd(Bsgly\text{-}N,O)_2]$, 125303-17-5.

Supplementary Material Available: Tables of full crystallographic data collection and reduction and structure refinement parameters, atomic temperature factors, hydrogen atom parameters, angles and distances associated with the toluene ring, selected least-squares planes, and selected IR data (5 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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(6) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101, 149–150.

(7) Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(8) Sheldrick, G. M. *SHELX 76 program for crystal structure determination*; University Chemical Laboratory: Cambridge, England, 1976.

(9) Vagg, R. S. *Acta Crystallogr., Sect. B* **1979**, *B35*, 341.

(10) Ito, T.; Marumo, F.; Saito, Y. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1062.

(11) (a) Jarzab, T. C.; Hare, C. R.; Langs, D. A. *Cryst. Struct. Commun.* **1973**, *3*, 395. (b) *Ibid.* **1973**, *3* 399.

(12) Sabat, M.; Jezowska, M.; Kozlowski, H. *Inorg. Chim. Acta* **1979**, *37*, L511.

(13) Antolini, L.; Menabue, L. *Inorg. Chem.* **1984**, *23*, 1418.

(14) Antolini, L.; Battaglia, L. P.; Bonamartini Corradi, A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Am. Chem. Soc.* **1985**, *107*, 1369.

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A Catenated Dinickel–Molybdenum Species Containing a Molybdenacyclopentadiene Unit Linked to a Dinickelatetrahedrane: An Example of η^5-Pentamethylcyclopentadienyl Group Lability

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Recently we reported the isolation of the side-bound ketone complexes CpM(R–C(O)–R′) [R = $C_{18}H_{21}$, R′ = $C_{25}H_{18}O$; M = Mo (**1**), W][1] from the reaction of Cp*Ni(CO)I, $[CpM(CO)_3]^-$, and PhC_2H.[2] The tungsten species (Figure 1) was structurally characterized. The mode of formation of these complexes remains obscure. As a nickel atom must eliminate a Cp* ligand at some stage and as these species have never been obtained in the absence of nickel, we believed that alkyne coupling occurs at a coordinatively unsaturated nickel center, followed by eventual transfer of the tropone ligand to the group 6 metal.[3] Addition of PhC_2H to a cold suspension of the thermally unstable Cp*Ni(CO)I,[4] followed by warming to ambient temperatures, would generate vacant coordination sites by ligand loss, which would enhance alkyne linkage. Subsequent addition of $[CpMo(CO)_3]^-$ would then afford **1** in improved yields. While testing the viability of this hypothesis, we isolated a trimetallic complex whose structure is presented here.

Discussion

Excess PhC_2H was added to a cold suspension of Cp*Ni(CO)I, the mixture was warmed, and $[CpMo(CO)_3]^-$ was subsequently added. After workup, $Cp^*Ni(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)Mo(CO)_2Cp$ (Ni–Mo) (**2**) and $Cp^*Ni\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(H)C(Ph)\}Mo(CO)_2Cp$ (Ni–Mo) (**3**)[2] were isolated. Small quantities of **1** formed, but yields were not significantly higher than reported,[2] and another product (**4**) was obtained in moderate yield. Scheme I shows the reaction sequence.

Aromatic signals and the Cp and Cp* resonances seen in the ^1H NMR spectrum hint that nickel and molybdenum are present and that **4** contains three PhC_2H groups. The CH protons appear as a singlet and two multiplets, indicating that one CH group does not couple to other protons. IR spectra exhibit two terminal $\nu(CO)$ bands; MS data reveal a parent ion with an *m/e* ratio of 776 amu. This agrees (with hindsight) with **4** having the empirical formula $Ni_2Mo(CO)_2(PhC_2H)_3CpCp^*$. Calculated isotopic envelopes closely match experimental values.

As the structure of **4** was not apparent, an X-ray diffraction study was undertaken. Tables I–IV list key data collection parameters, positional and isotropic thermal parameters for the heavy atoms and selected bond lengths and angles, respectively. An ORTEP diagram is shown in Figure 2.

4 contains a slightly bent Mo—Ni—Ni chain [Mo—Ni(2)—Ni(3) = 160.37 (2)°] and a molybdenacyclopentadiene Mo—C(Ph)=C(H)—C(H)=C(Ph) ring, derived from head-to-head coupling of two PhC_2H ligands. Every atom of the MoC_4 ring is linked to Ni(2), which in turn is bonded to Ni(3) [Ni(2)—Ni(3) = 2.3843 (5) Å]. The molybdenum atom is tilted out of the C_4 plane, 11° away from Ni(2). The Ni(2)—Mo distance of 2.6731 (4) Å is long: a Ni—Mo bond of 2.5859 (2) Å is noted in $CpNi\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C(Me)C(Me)\}Mo(CO)_2(\eta^5\text{-}C_5H_4Me)$.[5] The Mo—C bonds in the MoC_4 ring (2.197 Å, average) are normal Mo—C single bonds, and the C(12)—C(13) and C(14)—C(15) bonds (1.376 Å, average) are shorter than the other

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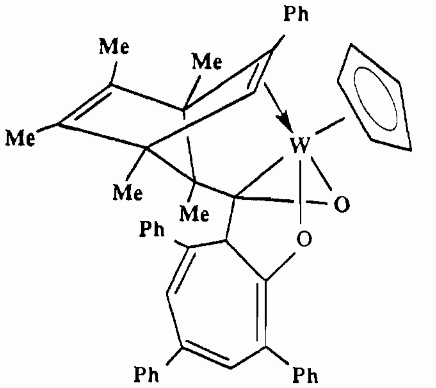
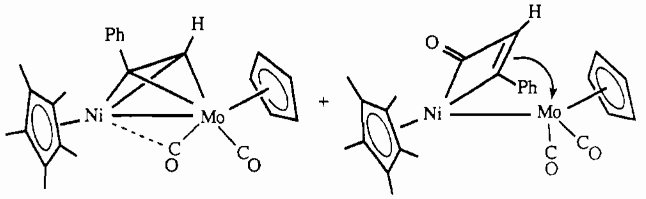


Figure 1. Schematic diagram of the ketone complex CpW[R-C(O)-R] (R = $C_{25}H_{18}O$, R' = $C_{18}H_{21}$), the tungsten analogue of **1**.

Scheme I

$Cp^*Ni(CO)I$ + excess PhC_2H + $[CpMo(CO)_3]^-$ ⟶ **1** + **4** +



2 **3**

Table I. Crystal and Data Collection Parameters for **4**

formula	$MoNi_2C_{41}H_{38}O_2$	fw	776.12
a, Å	11.933 (2)	space group	$P\bar{1}$
b, Å	12.354 (1)	T, °C	20
c, Å	13.415 (2)	λ, Å	0.71073
α, deg	89.48 (1)	d_{calcd}, g cm^{-3}	1.474
β, deg	71.37 (1)	linear abs coeff, cm^{-1}	14.5
γ, deg	69.924 (9)	transm coeff (min, max)	0.65, 1.00
V, Å^3	1748.8 (5)	$R(F_o)$	0.029
Z	2	$R_w(F_o)$	0.040

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.13247 (2)	0.00436 (2)	0.20318 (2)	3.282 (6)
Ni(2)	0.21025 (3)	0.16805 (3)	0.25449 (3)	3.065 (9)
Ni(3)	0.34552 (4)	0.27124 (4)	0.25732 (3)	3.70 (1)
O(21)	0.0687 (3)	0.1813 (3)	0.0441 (2)	7.72 (9)
O(22)	0.3884 (3)	−0.0575 (3)	0.0156 (2)	7.11 (9)
C(1)	−0.0314 (4)	−0.0519 (4)	0.1972 (4)	7.5 (1)
C(2)	0.0816 (4)	−0.1300 (4)	0.1267 (4)	6.5 (1)
C(3)	0.1537 (4)	−0.1883 (3)	0.1865 (4)	6.1 (1)
C(4)	0.0886 (4)	−0.1481 (3)	0.2934 (4)	6.0 (1)
C(5)	−0.0279 (4)	−0.0625 (4)	0.3003 (4)	6.9 (1)
C(12)	0.0314 (3)	0.1549 (3)	0.3259 (2)	3.50 (8)
C(13)	0.0834 (3)	0.1542 (3)	0.4039 (2)	3.86 (8)
C(14)	0.2071 (3)	0.0689 (3)	0.3856 (2)	3.97 (8)
C(15)	0.2591 (3)	−0.0047 (3)	0.2928 (2)	3.48 (7)
C(21)	0.0888 (3)	0.1215 (3)	0.1070 (3)	4.9 (1)
C(22)	0.2969 (3)	−0.0337 (3)	0.0868 (3)	4.63 (9)
C(31)	0.2245 (3)	0.3031 (3)	0.1868 (2)	3.45 (7)
C(32)	0.3250 (3)	0.2095 (3)	0.1393 (3)	3.71 (8)
C(51)	0.3461 (4)	0.3430 (4)	0.3980 (3)	6.7 (1)
C(52)	0.3599 (3)	0.4173 (3)	0.3212 (4)	6.4 (1)
C(53)	0.4697 (4)	0.3571 (4)	0.2366 (3)	6.9 (1)
C(54)	0.5251 (3)	0.2498 (4)	0.2646 (4)	6.7 (1)
C(55)	0.4503 (4)	0.2385 (4)	0.3625 (3)	7.2 (1)
C(121)	−0.0982 (3)	0.2381 (3)	0.3415 (3)	3.73 (8)
C(122)	−0.1244 (3)	0.3232 (3)	0.2742 (3)	4.69 (9)
C(123)	−0.2460 (3)	0.4007 (3)	0.2930 (3)	5.4 (1)
C(124)	−0.3443 (3)	0.3948 (4)	0.3765 (3)	5.6 (1)
C(125)	−0.3225 (3)	0.3127 (4)	0.4435 (3)	6.0 (1)
C(126)	−0.1994 (3)	0.2336 (4)	0.4269 (3)	5.1 (1)
C(151)	0.3886 (3)	−0.0931 (3)	0.2674 (2)	3.73 (8)
C(152)	0.4955 (4)	−0.0727 (4)	0.2102 (4)	6.8 (1)
C(153)	0.6159 (4)	−0.1565 (4)	0.1858 (4)	7.5 (1)
C(154)	0.6314 (4)	−0.2624 (4)	0.2194 (3)	5.8 (1)
C(155)	0.5259 (4)	−0.2851 (4)	0.2759 (4)	8.0 (1)
C(156)	0.4067 (7)	−0.2020 (4)	0.2986 (4)	7.0 (1)
C(311)	0.1463 (3)	0.4141 (3)	0.1649 (2)	3.48 (7)
C(312)	0.0476 (3)	0.4934 (3)	0.2444 (3)	4.65 (9)
C(313)	−0.0225 (4)	0.5991 (3)	0.2235 (3)	5.8 (1)
C(314)	0.0022 (4)	0.6289 (3)	0.1234 (3)	6.3 (1)
C(315)	0.0988 (5)	0.5538 (4)	0.0437 (3)	7.3 (1)
C(316)	0.1725 (4)	0.4450 (4)	0.0623 (3)	5.8 (1)
C(511)	0.2434 (6)	0.3670 (7)	0.5044 (5)	17.6 (2)
C(521)	0.2698 (6)	0.5408 (5)	0.3306 (7)	16.6 (2)
C(531)	0.5202 (6)	0.4067 (6)	0.1343 (5)	17.2 (2)
C(541)	0.6529 (5)	0.1632 (7)	0.1988 (6)	16.3 (2)
C(551)	0.4826 (6)	0.1357 (6)	0.4224 (5)	16.7 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

C—C bond in the MoC_4 ring [C(13)—C(14) = 1.434 (4) Å], as seen in other such systems. Ni(2)—C_{MoC_4} bonds are typical of coordinated olefins (2.12 Å, average).

A PhC_2H ligand perpendicularly bridges the Ni—Ni bond so the core of **4** can be described as a $NiMoC_4$ pentagonal pyramid that shares its apical Ni vertex with a Ni_2C_2 tetrahedron. The Ni—C bonds (1.90 Å, mean) are typical of Ni—C_{RC_2R} bonds noted in other molecules.[5,6] Coordination spheres of the outer metals in the chain are completed by two terminal CO groups and a Cp ligand for the Mo atom and by a Cp* group for Ni(3). Mo—C_{Cp} and Ni(3)—C_{Cp^*} distances are normal and unremarkable. Figure 3 shows another view of **4**.

Metals of groups 4,[7] 6,[8] 7,[9] 8,[10] 9,[11] and 10[12] form species containing metallacyclopentadiene groups. Head-to-tail and head-to-head alkyne linkages have been noted, but mixed-metal examples are less common. These include the compounds $Cp(CO)_2M\{\mu\text{-}\eta^4\text{-}CR{=}CR{-}CR{=}CR\}Co(CO)_2$ (R = CF_3; M = Mo, W),[13] $(OC)_3Co\{\mu\text{-}\eta^4\text{-}C(Ph){=}C(Me){-}C(Me){=}C(Ph)\}Mn(CO)_3$,[14] $(PhC_2H)Rh\{\mu\text{-}\eta^4\text{-}C(Ph){=}C(H){-}C(H){=}C(Ph)\}(\mu\text{-}P^tBu_2)Fe(CO)_2$,[15] and others.[10e,f,11a,12a]

The only crystallographically characterized species[16] containing

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(1) Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5.

(2) Chetcuti, M. J.; Fanwick, P. E.; Grant, B. E. *J. Am. Chem. Soc.* **1989**, *111*, 2743.

(3) The regio- and stereoselective insertion of PhC_2H into nickel(II) acyl species has been described recently: Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1989**, *8*, 967.

(4) Mise, T.; Yamazaki, H. *J. Organomet. Chem.* **1979**, *164*, 391.

(5) Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298.

(6) A Ni–C (mean) distance of 1.911 Å is noted in the complex $CoNi(CO)_3(\mu\text{-}C^2,\eta^2\text{-}PhC_2H)Cp$: Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyres, K. G. *Inorg. Chem.* **1980**, *19*, 693.

(7) (a) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1977**, *132*, 223. (b) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470. (c) Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1984**, *276*, 21. (d) Bickley, D. G.; Hao, N.; Bougeard, P.; Sayer, B. G.; Burns, R. C.; McGlinchey, M. J. *J. Organomet. Chem.* **1983**, *246*, 257. (e) Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65.

(8) (a) Knox, S. A. R.; Stansfield, R. D. F.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221. (b) Knox, S. A. R.; Stansfield, R. D. F.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1978**, 221. (c) Slater, S.; Muetterties, E. *Inorg. Chem.* **1980**, *19*, 3337; **1981**, *20*, 946. (d) Chisholm, M. H.; Eichorn, B. W.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, *861*. (e) Chisholm, M. H.; Conroy, B. K.; Huffman, J. C. *Organometallics* **1986**, *5*, 2384. (f) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806. (g) Green, M.; Kale, P. A.; Mercer, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 375. (h) Davidson, J. L.; Davidson, K.; Lindsell, W. E.; Murrall, N. W.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1677. (i) Carroll, W. E.; Green, M.; Orpen, A. G.; Schaverian, C. J.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1986**, 1021.

(9) (a) Pourreau, D. B.; Whittle, R. R.; Geoffroy, G. L. *J. Organomet. Chem.* **1984**, *273*, 333. (b) Leyendecker, M.; Sheldrick, W. S.; Kreiter, C. G. *J. Organomet. Chem.* **1984**, *270*, C37.

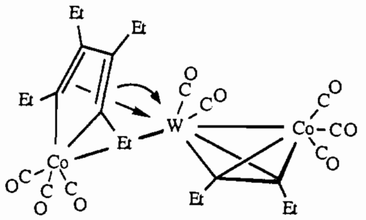
Table III. Selected Bond Distances (Å) for **4** with Esd's in Parentheses

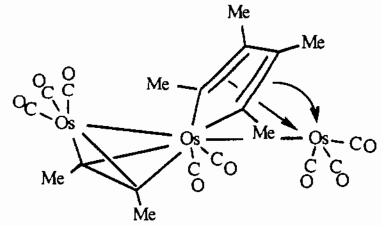
Mo(1)–Ni(2)	2.6731 (4)	Ni(2)–Ni(3)	2.3843 (5)
Mo(1)–C(12)	2.207 (3)	Mo(1)–C(15)	2.187 (3)
Mo(1)–C(21)	1.977 (4)	Mo(1)–C(22)	1.983 (4)
Ni(2)–C(12)	2.104 (3)	Ni(2)–C(13)	2.138 (3)
Ni(2)–C(14)	2.132 (3)	Ni(2)–C(15)	2.116 (3)
Ni(2)–C(31)	1.925 (3)	Ni(2)–C(32)	1.907 (3)
Ni(3)–C(31)	1.900 (3)	Ni(3)–C(32)	1.883 (3)
O(21)–C(21)	1.145 (4)	O(22)–C(22)	1.145 (4)
C(12)–C(13)	1.374 (4)	C(12)–C(121)	1.482 (4)
C(13)–C(14)	1.434 (4)	C(14)–C(15)	1.378 (4)
C(15)–C(151)	1.486 (4)	C(31)–C(32)	1.325 (4)
C(31)–C(311)	1.459 (4)		
Mo–C(Cp)	2.322 (22)	Ni–C(Cp*)	2.092 (22)
C(Cp)–C(Cp)	1.395 (8)	C(Cp*)–C(Cp*)	1.385 (15)
C(Cp*)–C(Me)	1.518 (10)	C(Ph)–C(Ph)	1.376 (17)

Table IV. Selected Bond Angles (deg) for **4** with Esd's in Parentheses

Ni(2)–Mo(1)–C(12)	49.95 (7)	Ni(2)–Mo(1)–C(15)	50.40 (8)
Ni(2)–Mo(1)–C(21)	77.5 (1)	Ni(2)–Mo(1)–C(22)	79.7 (1)
C(12)–Mo(1)–C(15)	74.2 (1)	C(12)–Mo(1)–C(21)	83.6 (1)
C(12)–Mo(1)–C(22)	129.1 (1)	C(15)–Mo(1)–C(21)	125.9 (1)
C(15)–Mo(1)–C(22)	79.1 (1)	C(21)–Mo(1)–C(22)	78.1 (1)
Mo(1)–Ni(2)–Ni(3)	160.37 (2)	Mo(1)–Ni(2)–C(12)	53.44 (8)
Mo(1)–Ni(2)–C(15)	52.80 (8)	Mo(1)–Ni(2)–C(31)	130.16 (8)
Mo(1)–Ni(2)–C(32)	115.22 (9)	Ni(3)–Ni(2)–C(31)	50.98 (8)
Ni(3)–Ni(2)–C(32)	50.57 (9)	C(12)–Ni(2)–C(31)	120.4 (1)
C(12)–Ni(2)–C(32)	149.5 (1)	C(13)–Ni(2)–C(31)	130.3 (1)
C(13)–Ni(2)–C(32)	166.6 (1)	C(14)–Ni(2)–C(31)	151.2 (1)
C(14)–Ni(2)–C(32)	141.1 (1)	C(15)–Ni(2)–C(31)	160.3 (1)
C(15)–Ni(2)–C(32)	120.0 (1)	C(31)–Ni(2)–C(32)	40.4 (1)
Ni(2)–Ni(3)–C(31)	51.91 (9)	Ni(2)–Ni(3)–C(32)	51.47 (9)
C(31)–Ni(3)–C(32)	41.0 (1)	Mo(1)–C(12)–Ni(2)	76.60 (9)
Mo(1)–C(12)–C(13)	115.3 (2)	Mo(1)–C(12)–C(121)	124.1 (2)
C(13)–C(12)–C(121)	119.1 (3)	C(12)–C(13)–C(14)	116.3 (3)
C(13)–C(14)–C(15)	116.2 (3)	Mo(1)–C(15)–Ni(2)	76.80 (9)
Mo(1)–C(15)–C(14)	116.1 (2)	Mo(1)–C(15)–C(151)	124.5 (2)
C(14)–C(15)–C(151)	119.0 (3)	Mo(1)–C(21)–O(21)	173.9 (3)
Mo(1)–C(22)–O(22)	175.7 (3)	Ni(2)–C(31)–Ni(3)	77.1 (1)
Ni(2)–C(31)–C(32)	69.1 (2)	Ni(3)–C(31)–C(32)	68.8 (2)
C(32)–C(31)–C(311)	141.4 (3)	Ni(2)–C(32)–Ni(3)	78.0 (1)
Ni(2)–C(32)–C(31)	70.5 (2)	Ni(3)–C(32)–C(31)	70.2 (2)

a structural core mirroring that in **4** is the species $(OC)_3Co\{\mu\text{-}\eta^4\text{-}C(Et){=}C(Et){-}C(Et){=}C(Et)\}W(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}EtC_2Et)Co(CO)_3$ isolated as the major product when $Co_2(CO)_8$ was treated with $W(CO)(EtC_2Et)_3$.[17] The central, not the terminal, osmium forms part of a metallacyclopentadiene ring in the Os_3 species $(OC)_3Os\{\mu\text{-}\eta^4\text{-}C(Me){=}C(Me){-}C(Me){=}C(Me)\}Os(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}MeC_2Me)Os(CO)_3$.[18] The trimetal angle in each case is less than 180° [153.6 (1)° for Co—W—Co; 152.5° (average) for Os—Os—Os; 160.37 (2)° for **4**].





Metals bind tightly to π-coordinated Cp ligands, and cleavage of such bonds is rare.[19] Lability of these ligands is commonly observed only in paramagnetic metallocene chemistry and/or under strongly reducing conditions.[20] Cp* ligands appear to be more labile than their Cp congeners, and stripping of Cp* ligands off metals is not unprecedented under mild conditions. This lability may arise from the greater steric bulk of these ligands. Small quantities of C_5Me_5H and its dimer are frequently observed in reactions involving Ni—Cp* complexes,[21] and cleavage of Cp*—metal bonds has been reported in reactions of iridium,[11h] tungsten,[22] yttrium,[23] and thorium[24] complexes.

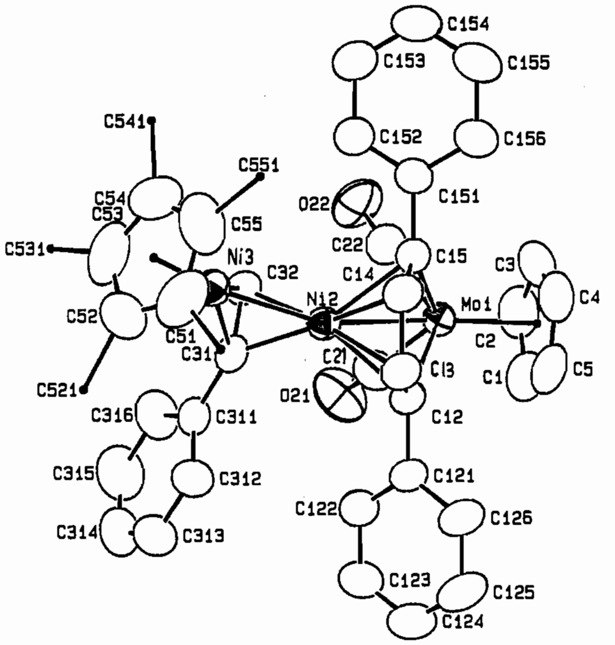


Figure 2. ORTEP diagram of **4** showing 50% probability ellipsoids and the numbering scheme. Cp* methyl carbon ellipsoids are depicted as small circles of arbitrary radius, and hydrogen atoms are omitted for clarity.

Experimental Section

X-ray Data Collection. Purple-red crystals of **4** were grown from hexane at −20 °C. A single crystal was selected and mounted on an Enraf-Nonius CAD 4 diffractometer at 20 ± 1 °C. Cell constants and an orientation matrix were obtained from least-squares refinement using setting angles of 25 reflections with $22 < \theta < 23°$. There were no systematic absences, and the space group was determined to be $P\bar{1}$ (No. 2). As a check on crystal and electronic stability, three representative reflections were measured every 83 min. Within experimental error, no decay was observed.

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(10) (a) Detlaff, G.; Weiss, E. *J. Organomet. Chem.* **1976**, *108*, 213. (b) Prince, S. R. *Cryst. Struct. Commun.* **1976**, *5*, 451. (c) Bühler, R.; Geist, R.; Mündnich, R.; Plieninger, H. *Tetrahedron Lett.* **1973**, 1919. (d) Omori, H.; Suzuki, H.; Yoshihiko, M. *Organometallics* **1989**, *8*, 1576. (e) King, M.; Holt, E. M.; Radnia, P.; Mckennis, J. S. *Organometallics* **1982**, *1*, 1718. (f) Bruce, R.; Moseley, K.; Maitlis, P. M. *Can. J. Chem.* **1967**, *45*, 2011. Epstein, E. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 502. (g) Bruce, M. I.; Matisons, J. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1983**, *251*, 149. (h) Astier, A.; Duran, J. C.; Jeannin, Y.; Rigault, C. *J. Organomet. Chem.* **1983**, *241*, 53.

(11) (a) Yamazaki, H.; Yasufuku, K.; Wakatsuki, Y. *Organometallics* **1983**, *2*, 726. An extensive listing of metallacyclopentadiene complexes is included here. (b) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157. (c) McAlistair, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666. (d) Gastinger, R. G.; Rausch, M. D.; Sullivan, D. A.; Palenik, G. J. *J. Am. Chem. Soc.* **1976**, *98*, 719. (e) Bainbridge, C. W.; Dickson, R. S.; Fallon, G. D.; Grayson, I.; Nesbit, R. J.; Weigold, J. *Aust. J. Chem.* **1986**, *39*, 1187. (f) Gardner, S. A.; Andrews, P. S.; Rausch, M. D. *Inorg. Chem.* **1973**, *12*, 2396. (g) Dickson, R. S.; Kirsch, H. P. *Aust. J. Chem.* **1972**, *25*, 2535. (h) Corrigan, P. A.; Dickson, R. S.; Fallon, G. D.; Michel, L. J.; Mok, C. *Aust. J. Chem.* **1978**, *31*, 1937. (i) McDonnell-Bushnell, L. P.; Evitt, E. R.; Bergman, R. G. *J. Organomet. Chem.* **1978**, *157*, 445. (j) Müller, J.; Hänsch, C.; Pickardt, J. *J. Organomet. Chem.* **1983**, *259*, C21.

(12) (a) Colbran, S. B.; Robinson, B. R.; Simpson, J. *Organometallics* **1985**, *4*, 1594. (b) Pörschke, K. R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1288.

(13) (a) Davidson, J. L.; Manojlovic-Muir, K. W.; Keith, A. N. *J. Chem. Soc., Chem. Commun.* **1981**, 749. (b) Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

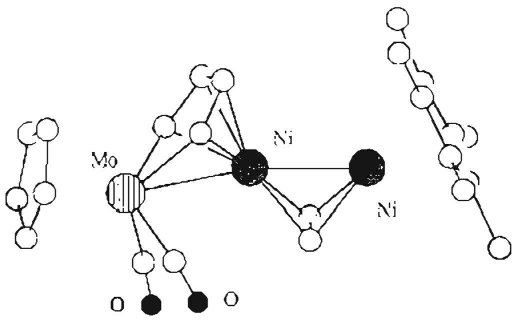

Figure 3. Alternative view of **4**. Phenyl groups and hydrogen atoms are omitted for clarity. Carbon atoms bearing phenyl ligands are shown as dotted circles; other carbon atoms, as empty circles.

After Lorentz and polarization corrections, the structure was solved on a VAX computer using SHELX-86. Remaining atoms were located by using DIRDIF and in succeeding difference Fourier syntheses. Only data with $I > 3\sigma(I)$ were used in the refinement; an absorption correction[24] was applied. Hydrogen atoms were located and added to structure factor calculations but were not refined. Scattering factors[25] and anomalous dispersion effects[26] were included in F_c. Refinement converged at $R = 0.029$ and $R_w = 0.040$. The highest peak in the final difference Fourier map had a height of 0.41 e/Å^3, with an estimated error based on ΔF of 0.06.

Syntheses and Spectroscopic Data. Manipulations were performed under N_2 by using standard Schlenk techniques. CH_2Cl_2 was distilled over CaH_2; other solvents were distilled over sodium benzophenone ketyl. $[CpMo(CO)_3]^-$ was prepared by reducing $[CpMo(CO)_3]_2$ with $KBHEt_3$ (Aldrich). ^1H and ^{13}C NMR spectra were obtained on a GE GN-300 spectrometer in chloroform-d_1; chemical shifts (ppm) are relative to the traces of $CHCl_3$ present or to the solvent's ^{13}C NMR signal. Coupling constants are in Hz. IR spectra (cm^{-1}) were recorded on an IBM FT-IR 32 spectrometer. Mass spectra were obtained on a Finnegan Matt instrument; the reference nuclei for HRMS data were ^{58}Ni and ^{98}Mo. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

(a) Synthesis of 1–4. PhC_2H (1.4 mL, 13 mmol) was added to a suspension of freshly prepared[4] Cp*Ni(CO)I (1050 mg, 3 mmol) and the brown slurry was warmed to 0 °C and stirred for 1 h. $[CpMo(CO)_3]$ (15 mL of a 0.17 M THF solution) was added and the mixture stirred for a further 5 h at ambient temperature, concentrated, filtered through a Celite pad, and pumped dry. The residue was extracted with hexanes and the resulting solution subjected to chromatography on silica gel. **2** eluted as a red-brown band with hexanes/ether (5:1); **4** (a purple band) and **1** (a blue-purple band) eluted with ether/hexanes (1:1). After hexanes extraction, the residue was extracted with toluene. Chromatography on silica gel and elution with dichloromethane afforded **3**. Yields: **1**, ≈45 mg (2%); **2**, 62 mg (4%); **3**, 617 mg (38%); **4**, 140 mg (6%).

(b) Spectroscopic Data for 1. ^1H NMR: δ 7.72–7.00 (m, 20 H, *Ph*), 7.21 (H, C*H*), 6.23 (H, C*H*), 5.83 (5 H, C_5H_5), 3.51 (H, C*H*), 2.62 (H, C*H*), 1.50 (q, 3 H, *Me*, $J_{Me-Me} = 1.2$), 1.39 (3 H, *Me*), 1.22 (3 H, *Me*), 1.03 (q, 3 H, *Me*, J_{Me-Me} 1.2), 0.57 (3 H, *Me*). MS: *m/e* 762 (M^+).

(c) Spectroscopic Data for 2. ^1H NMR: δ 7.33–7.19 (m, 5 H, C_6H_5), 5.43 (H, C*H*), 5.12 (5 H, C_5H_5), 1.53 (15 H, C_5Me_5). $^{13}C\{^1H\}$ NMR (assigned from ^1H-coupled data): δ 240.9, 230.3 (2 *C*O), 140.7 [C(1), *Ph*], 130.6 [C(3) and C(5), *Ph*], 127.9 [C(2) and C(6), *Ph*], 126.6 [C(4), *Ph*], 100.7 (C_5Me_5), 99.1 (*C*Ph), 92.2 (C_5H_5), 75.8 (*C*H), 8.4 (C_5Me_5). IR (THF): 1950 (s), 1910 (m), 1821 (m, br). MS: *m/e* 514 (M^+), 486 [$(M - CO)^+$], 458 [$(M - 2CO)^+$], 356 [$(M - 2CO - PhC_2H)^+$]. HRMS: calcd for $C_{25}H_{26}MoNiO_2$, 514.0340; found, 514.0333.

(d) Spectroscopic Data for 3. ^1H NMR: δ 7.31 [H, C*H*C(O)], 7.27–6.96 (m, 5 H, C_6H_5), 5.35 (5 H, C_5H_5), 1.78 (15 H, C_5Me_5). ^{13}C NMR: δ 232.4, 231.6 (2 *C*O), 172.9 (Ni–*C*O), 139.4 [C(1), *Ph*], 127.9 [C(2) and C(6) or C(3) and C(5), *Ph*], 125.4 [C(3) and C(5) or C(2) and C(6), *Ph*], 123.4 [C(4), *Ph*], 102.3 (C_5Me_5), 91.9 (C_5H_5), 67.4 (*C*Ph), 9.0 (C_5Me_5). IR (THF): 1953 (s), 1842 (s), 1690 (m, Ni–CO). MS: *m/e* 514 [$(M - CO)^+$], 486 [$(M - 2CO)^+$], 458 [$(M - 3CO)^+$] (M^+ not seen: **3** is readily thermally decarbonylated to **2**). Anal. Calcd for $C_{26}H_{26}MoNiO_3$: C, 57.71; H, 4.84. Found: C, 57.67; H, 4.98.

(e) Spectroscopic Data for 4. ^1H NMR: δ 7.40–6.95 (m, 15 H, C_6H_5), 6.48 (d, H, C*H*=CH, $J_{HH} = 2.5$), 6.31 (d, H, CH=C*H*, $J_{HH} = 2.5$), 5.25 (H, μ-PhC_2H), 4.72 (5 H, C_5H_5), 1.55 (15 H, C_5Me_5). IR (hexanes): 1973 (vs), 1918 (s). IR (Nujol): 1970 (s), 1903 (s). MS: *m/e* 776 (M^+). HRMS: calcd for $C_{41}H_{38}MoNi_2O_2$, 776.0620; found, 776.0621.

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Supplementary Material Available: For **4**, a graph of calculated and experimental isotopomer patterns for the parent molecular ion of **4** and full tables of crystal and data collection parameters, bond lengths and angles, hydrogen atom positional parameters, and anisotropic thermal parameters for the heavy atoms (13 pages); structure factor listings (29 pages). Ordering information is given on any current masthead page.

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(14) Einstein, F. W. B.; Manning, P.; Peterson, L. K.; Tyers, K. G. *Inorg. Chim. Acta* **1986**, *111*, L49.

(15) Arif, A. M.; Chandler, D. J.; Jones, R. A. *Organometallics* **1987**, *6*, 506.

(16) The Ni_3 species $CpN\overline{i\{\mu\text{-}\eta^4\text{-}C(CF_3){=}C(CF_3){-}C(CF_3){=}C}(CF_3)\}Ni(\mu\text{-}\eta^2,\eta^2\text{-}CF_3C_2CF_3)NiCp$ is proposed to have a structure similar to that of **4** on the basis of spectroscopic evidence: Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1123.

(17) (a) Farrugia, L. J.; Went, M. J. *Chem. Soc., Chem. Commun.* **1987**, 973. (b) Scott, I. D.; Smith, D. O.; Went, M. J.; Farrugia, L. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1375.

(18) Johnson, B. F. G.; Khattar, R.; Lahoz, F. J.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1987**, *335*, C17.

(19) An example is the slippage of a η^5-C_5H_5 ligand to an η^1 and ultimately an η^0 (ionic) bonding mode: Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241.

(20) Jonas, K. *Adv. Organomet. Chem.* **1982**, *19*, 97.

(21) Chetcuti, M. J.; Grant, B. E. Unpublished observations.

(22) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391.

(23) Finke, R. G.; Keenan, S. R.; Watson, P. L. *Organometallics* **1989**, *8*, 263.

(24) Ryan, R. R.; Salazar, K. V.; Sauer, N. N.; Ritchey, J. M. *Inorg. Chim. Acta* **1989**, *162*, 221.

(25) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(26) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(27) (a) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781. (b) Reference 26, Table 2.3.1.