Table IV. Electrochemical and Electronic Absorption Spectra Data for *cis*-$[Re_2(O_2CR)_2X_2(Ph_2Ppy)_2]^{n+}$ (n = 0, 1)

complex	elect abs spectrum, nm[a]	voltammetric half-wave potentials, V[a]	
		$E_{1/2}$(ox(2))[c]	$E_{1/2}$(ox(1))[c]
cis-$Re_2(O_2CC_2H_5)_2Cl_2(Ph_2Ppy)_2$	720 sh, 618 (5500), 541 (4300), 384 (4500), 345 (4300), 248 sh	+1.18 (110)	+0.10 (110)
cis-$Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2$	720 sh, 617 (6100), 543 (5100), 385 (5100), 348 (5000), 245 sh	+1.20 (120)	+0.11 (110)
cis-$Re_2(O_2CC_2H_5)_2Br_2(Ph_2Ppy)_2$	735 sh, 617 (4400), 538 (3400), 380 (3600), 340 sh, 285 sh, 255 sh	+1.22 (130)	+0.14 (120)
cis-$[Re_2(O_2CC_2H_5)_2Cl_2(Ph_2Ppy)_2]PF_6$	510 (3400), 390 sh, 356 (5500), 300 sh, 260 sh	+1.18 (120)	+0.10 (120)[d]
cis-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]PF_6$	505 (3500), 395 sh, 357 (5900), 300 sh, 260 sh	+1.20 (120)	+0.13 (120)[d]

[a] Measured in CH_2Cl_2; ϵ_{max} values in parentheses. [b] Versus Ag/AgCl. Recorded on solutions in 0.1 M $TBAH/CH_2Cl_2$ by the use of a Pt-bead electrode; data obtained at v = 200 mV/s. Under our experimental conditions $E_{1/2}$ for the ferrocenium/ferrocene couple was +0.47 V vs Ag/AgCl. [c] Numbers in parentheses are ΔE_p values (i.e., $E_{p,a} - E_{p,c}$). [d] $E_{1/2}$(red) values.

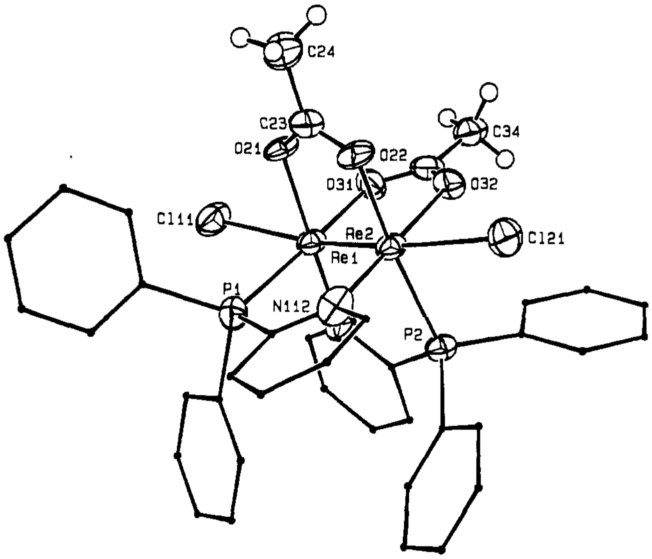

Figure 1. ORTEP view of the structure of the *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]^+$ cation. For clarity, the atomic numbering scheme is given for all atoms except the phenyl and pyridyl ring carbon atoms. the thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl and pyridyl rings, which are circles of arbitrary radius.

highly structured patterns that are centered at $g_\perp \simeq 2.82$ ($A_\perp \simeq 425$ G) and $g_\parallel \simeq 1.41$ ($A_\parallel \simeq 450$ G).

The conclusion that the complexes described in this report are correctly formulated as *cis*-$Re_2(\mu\text{-}O_2CR)_2X_2(\mu\text{-}Ph_2Ppy)_2$ has been confirmed by a crystal structure determination on the oxidized species *cis*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-}Ph_2Ppy)_2]PF_6$ (Figure 1). Important structural parameters are listed in Table III. Our attempts to grow suitable crystals of *cis*-$Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2$ were not successful. However, since the electrochemical properties of the oxidized complex and its neutral precursor are the same, except of course for the fact that the reversible couple at +0.10 V corresponds to a reduction in the case of the former complex and an oxidation for the latter (see Table IV), they must possess very similar structures. The structure of the *cis*-$[Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-}Ph_2Ppy)_2]^+$ cation is also very similar to that of the analogous dirhodium(II) complex *cis*-$Rh_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2$,[11] in which the individual sets of acetate and Ph_2Ppy ligands are cis to one another. Also, the two Ph_2Ppy ligands are arranged in a head-to-tail fashion. Of interest is a similar nonlinearity of the Cl–Re–Re–Cl and Cl–Rh–Rh–Cl units; the Re–Re–Cl and Rh–Rh–Cl angles are 165.0 (2) and 168.7 (1)°, respectively. The metal–metal distances in these two structures are of course quite different, with the Re–Re distance being 2.261 (1) Å and the Rh–Rh distance equal to 2.518 (1) Å; this in part reflects the different metal–metal bond orders, which are formally 3.5 and 1.0, respectively. An important consequence of this difference is the closer approach of the dirhenium structure to an ideal *eclipsed* conformation in order to maximize the δ component to the metal–metal bonding in the $\sigma^2\pi^4\delta^2\delta^{*1}$ configuration.[12] This is reflected by the torsional angles O(21)–Re(1)–Re(2)–O(22), O(31)–Re(1)–Re(2)–O(32), P(1)–Re(1)–Re(2)–N(112), and N(212)–Re(1)–Re(2)–P(2) being only 3.4 (6), 1.6 (6), 3.8 (6), and 0.7 (6)°, respectively. In contrast to this, the average torsional angle is much larger (15.5°) for the dirhodium complex.[11] This larger angle no doubt reflects the absence of any electronic barrier to rotation about the Rh–Rh single bond in the dirhodium complex.

The structure of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]PF_6$ also resembles closely those of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dppa)_2]PF_6$[4] and the neutral complexes *cis*-$Re_2(O_2CCH_3)_2Cl_2(LL)_2$ (LL = dppm, dppa).[3,4] The Re–Re distance for *cis*-$[Re_2(O_2CCH_3)_2Cl_2(dpa)_2]PF_6$ is 2.276 (1) Å, a value which is very close to that determined for its Ph_2Ppy analogue (2.261 (1) Å). It is also similar to the Re–Re distance of 2.270 (1) Å in the dirhenium(II) complex $Re_2Cl_4(Ph_2Ppy)_2)(PEt_3)$, a molecule that also contains cis bridging Ph_2Ppy ligands arranged head-to-tail.[2] The Re–P and Re–N distances in the structure of *cis*-$[Re_2(O_2CCH_3)_2Cl_2(Ph_2Ppy)_2]^+$ are ca. 2.40 (1) and ca. 2.14 (2) Å, respectively. These values accord with those reported in the structure determination of $Re_2Cl_4(Ph_2Ppy)_2)(PEt_3)$.

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Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1), positional parameters and their errors for the non-hydrogen atoms (Table S2) and for the hydrogen atoms (Table S3), thermal parameters (Table S4), bond distances (Table S5), and bond angles (Table S6) (16 pages); a table of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(11) Cotton, F. A.; Matusz, M. *Inorg. Chim. Acta* **1988**, *143*, 45.

(12) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

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Deprotonated Amide Nitrogen Coordinating to the Palladium(II) Ion. Crystal and Molecular Structure of Disodium Bis(*N*-tosylglycinato-*N*,*O*)palladate(II)

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Peptides and related ligands are able to bind several metal ions upon formation of one or more chelating rings involving up to three

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Table I. Crystallographic Data for $Na_2[Pd(Tsgly\text{-}N,O)_2]$[a]

cryst syst: triclinic	mol formula: $C_{18}H_{18}N_2Na_2O_8PdS_2$
a = 6.128 (1) Å	space group: $P\bar{1}$ C_i^1, No. 2)
b = 8.100 (1) Å	T = 20 °C
c = 10.666 (2) Å	λ = 0.71069 Å
α = 86.85 (1)°	mol wt: 606.672
β = 81.58 (1)°	ρ(obsd) = 1.92 g cm^{-3}, ρ(calcd) = 1.94 g cm^{-3}
γ = 86.33 (1)°	μ(Mo Kα) = 10.62 cm^{-1}
V = 522.12 Å^3	transm coeff: 0.92–0.99
Z = 1	$R = R_w$ = 2.58

[a] Unit cell parameters and their esd's were derived from a least-squares fit to the setting angles of 25 accurately centered reflections.

Table II. Final Positional Parameters

atom	x/a	y/b	z/c
Pd	0.0	0.0	0.0
Na	−0.2476 (2)	0.4665 (2)	−0.0735 (1)
S	0.2892 (1)	0.27833 (9)	−0.17569 (7)
O(1)	0.2036 (4)	−0.1998 (3)	−0.0172 (2)
O(2)	0.5175 (4)	−0.3112 (3)	−0.1108 (2)
O(3)	0.5174 (4)	0.3213 (3)	−0.2013 (2)
O(4)	0.1381 (4)	0.3951 (3)	−0.1041 (2)
N	0.2676 (4)	0.1017 (3)	−0.1057 (3)
C(1)	0.3861 (5)	−0.1915 (4)	−0.0921 (3)
C(2)	0.4351 (5)	−0.0242 (4)	−0.1576 (3)
C(3)	0.2005 (5)	0.2704 (4)	−0.3265 (3)
C(4)	0.3293 (6)	0.3257 (5)	−0.4351 (4)
C(5)	0.2550 (7)	0.3201 (5)	−0.5516 (4)
C(6)	0.0518 (6)	0.2567 (4)	−0.5591 (4)
C(7)	−0.0744 (6)	0.2005 (5)	−0.4993 (4)
C(8)	−0.0020 (6)	0.2066 (5)	−0.3318 (4)
C(9)	−0.0302 (8)	0.2519 (6)	−0.6857 (4)

deprotonated peptide nitrogens.[1] The deprotonation of the peptide nitrogen is promoted by the metal to a different extent following the order Pd(II) > Cu(II) > Ni(II) > Co(II). The same order holds for the metal-promoted deprotonation of the sulfonamide nitrogen in amino acids N-protected by a sulfonic group (Ar–SO_2–N(amino acid). Pd(II) is thus the most effective metal ion in substituting for the amide nitrogen bound hydrogen of both classes of ligands. A conspicuous amount of data is available on solution studies of Pd(II)–peptide and related systems,[1] whereas the X-ray investigations mostly deal with Pd(II)–bis(amino acidato) complexes[1] in which the ligands, cis to each other, bind in a bidentate fashion through the carboxylate and the amino groups, giving rise to the usual square-planar coordination.[1] No examples of ligands binding through a deprotonated amide nitrogen are available so far, though a structure with a deprotonated but uncoordinated amide nitrogen has been described.[2] In this note we report the crystal and molecular structure of a Pd(II) complex with the *N*-tosyl derivative of glycine (Tsgly hereafter), in which the ligand binds the metal ion in a bidentate fashion through the carboxylate oxygen and the deprotonated amide nitrogen. This binding mode was previously observed also for the Cu(II) ion.[3] Some properties of the Pd(II) complex of the related ligand *N*-(phenylsulfonyl)glycine (Bsgly hereafter) are also reported. The $Na_2[Pd(Tsgly\text{-}N,O)_2]$ (Tsgly-*N,O* = *N*-tosylglycinate dianion) species was separated with two different procedures: (a) 1 M HCl was added to a suspension of $PdCl_2$ (Janssen) (2 × 10^{-3} mol in 50 mL of water), yielding a red solution; 4 × 10^{-3} mol of *N*-tosylglycine dissolved in 25 mL of methanol at 50 °C was then added, and the pH was raised to 5.7 with concentrated NaOH. Upon cooling of the yellow solution at 20 °C, yellow-orange crystals separated. (b) A 2.5 × 10^{-3} mol amount of solid $Pd(NO_3)_2 \cdot 2H_2O$ (Fluka) was slowly added to 100 mL of an aqueous/methanolic (4:1 v/v) solution containing 10^{-2} mol of *N*-tosylglycine at pH 11 under fast stirring. The pH dropped to 3.5, and it was corrected to 6 with concentrated NaOH. After few days at room temperature, yellow-orange crystals separated. Anal. Calcd for $Na_2[Pd(Tsgly\text{-}N,O)_2]$, $C_{18}H_{18}N_2Na_2O_8PdS_2$: C, 35.62; H, 2.99; N, 4.62. Found: C, 35.70; H, 2.98; N, 4.63. The $Na_2[Pd(Bsgly\text{-}N,O)_2] \cdot H_2O$ (BsglyNO = *N*-(phenylsulfonyl)glycinate dianion) species was separated with the same procedures described above. Anal. Calcd for $C_{16}H_{16}N_2Na_2O_9S_2$: C, 32.18; H, 2.70; N, 4.79. Found: C, 32.11; H, 2.72; N, 4.62.

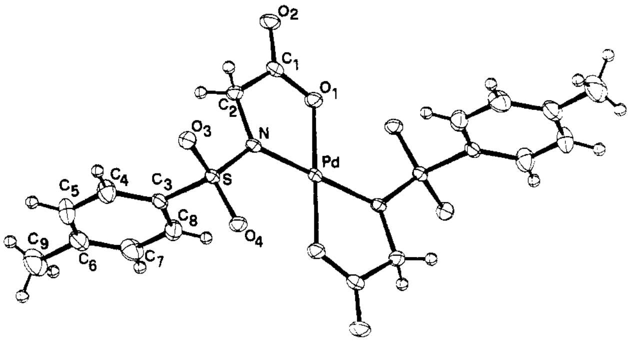

Figure 1. ORTEP view of the $[Pd(Tsgly\text{-}N,O)_2]^{2-}$ anion.

Table III. Selected Bond Distances (Å) and Angles (deg)[a]

Pd–O(1)	1.979 (2)	C(2)–N	1.470 (4)
Pd–N	2.042 (3)	N–S	1.581 (3)
C(1)–O(1)	1.279 (4)	S–O(3)	1.446 (2)
C(1)–O(2)	1.226 (4)	S–O(4)	1.448 (2)
C(1)–C(2)	1.517 (4)	S–C(3)	1.777 (4)
	Short Contacts		
Na–O(4)	2.376 (3)	Na–O(2)″	2.286 (3)
Na–O(1)′	2.334 (3)	Na–O(4)‴	2.449 (3)
Na–O(2)′	2.688 (3)	Na–O(3)⁗	2.506 (3)
O(1)–Pd–N	80.6 (1)	N–S–O(3)	111.1 (1)
O(1)–Pd–N′	99.4 (1)	N–S–O(4)	108.4 (1)
Pd–O(1)–C(1)	118.8 (2)	N–S–C(3)	108.5 (2)
Pd–N–C(2)	112.5 (2)	C(7)–C(8)–C(3)	118.9 (4)
O(1)–C(1)–O(2)	122.6 (3)	O(3)–S–O(4)	116.0 (1)
O(1)–C(1)–C(2)	116.7 (3)	C(3)–S–O(3)	105.8 (2)
O(2)–C(1)–C(2)	120.8 (3)	C(3)–S–O(4)	106.8 (2)
C(1)–C(2)–N	109.6 (3)	S–C(3)–C(4)	121.0 (3)
C(2)–N–S	114.1 (2)	S–C(3)–C(8)	118.3 (3)

[a] Equivalent positions: ′, $-x, -y, -z$; ″, $x - 1, y + 1, z$; ‴, $-x, -y + 1, -z$; ⁗, $x - 1, y, z$.

The crystallographic data, collected on a Enraf-Nonius CAD4 single-crystal diffractometer using graphite-monochromated Mo Kα radiation, were corrected for Lorentz and polarization effects, and an empirical absorption correction based on a ψ scan[4] was applied. Table I summarizes the details of crystal data collection and reduction. The structure was solved by conventional Patterson and Fourier techniques and refined through full-matrix least-squares calculation.[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as fixed contributors at locations obtained from difference map ($B_H = B_C + 1.0$ Å^2). Final R and R_w values were 2.58. A final difference map was featureless, with no peaks higher than 0.25 Å^{-3}. Complex neutral-atom scattering factors[6] were used throughout; major calculations were carried out on a VAX 11/750 computer using the SHELX-76 system of programs[7] and ORTEP plotting program.[8] Final

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(1) Pettit, L. D.; Bezer, M. *Coord. Chem. Rev.* **1985**, *61*, 97.

(2) Sheller-Krattiger, V.; Sheller, K. H.; Sinn, E.; Martin, R. B. *Inorg. Chim. Acta* **1982**, *60*, 45.

(3) Antolini, L.; Battaglia, L. P.; Battistuzzi Gavioli, G.; Bonamartini Corradi, A.; Grandi, G.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 4327.

(4) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

(5) The quantity minimized during refinement was $\sum w(|F_o| - |F_c|)^2$, where w is the weighted factor. The unweighted residuals are defined as follows: $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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.

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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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