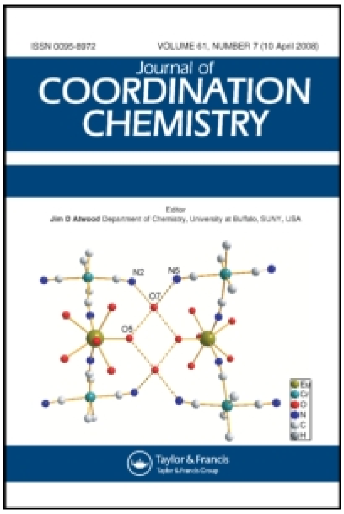

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HETEROBIMETALLIC COMPLEXES DERIVED FROM CYCLOPENTADIENYLCYANO (η^1-BIS(DIPHENYLPHOSPHINO)METHANE)NICKEL. THE CRYSTAL AND MOLECULAR STRUCTURE OF CYCLOPENTADIENYLNICKEL (μ-BIS(DIPHENYLPHOSPHINO) METHANE) CYANO(TRIPHENYLPHOSPHINE) PLATINUM

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HETEROBIMETALLIC COMPLEXES DERIVED FROM CYCLOPENTADIENYLCYANO (η^1-BIS(DIPHENYLPHOSPHINO)METHANE)NICKEL. THE CRYSTAL AND MOLECULAR STRUCTURE OF CYCLOPENTADIENYLNICKEL (μ-BIS(DIPHENYLPHOSPHINO) METHANE) CYANO(TRIPHENYLPHOSPHINE) PLATINUM

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The synthesis of $CpNi(\mu\text{-}DPPM)Pt(CN)(PPh_3)$ (**1**) (DPPM = bis(diphenylphosphino)methane) and the structures of **1** and of $CpNi(\mu\text{-}CN)(\mu\text{-}DPPM)Mo(CO)_4$ **2** are reported. There is a Pt - Ni bond (Pt - Ni = 2.5356(9) Å) in **1** and the presence of a bridging cyano ligand is confirmed in **2**. **1**: Monoclinic; $P2_1/n$; a = 14.182(1), b = 21.662(2), c = 15.125(1) Å, β = 105.29°; Z = 4; R = 0.034, R_W = 0.047 for 6230 reflections ($I \geq 3\sigma(I)$). **2**: Orthorhombic; Pbca; a = 19.762(3), b = 21.263(4), c = 15.422(3) Å; Z = 8; R = 0.054, R_W = 0.050 for 1901 reflections ($I \geq 2\sigma(I)$).

Keywords: nickel; platinum; molybdenum; dinuclear; heterobimetallic

INTRODUCTION

During our ongoing investigations into the directed synthesis of heterobimetallic complexes stabilized by bridging diphosphine ligands,[1–6] we have frequently encountered problems resulting from halide transfer from the 'metalloligands' used, *e.g.* $CpMCl(\eta^1\text{-}MeN(PF_2)_2)_2$(M = Fe, Ru), *fac*-$ReBr(CO)_3(\eta^1\text{-}L_2)_2$ ($L_2 = MeN(PF_2)_2$, $Me_2PCH_2PMe_2$), to the added, low-valent metal during complex formation. This has generally resulted in products showing very low subsequent reactivity. We were thus intrigued by the report that CpNi(CN) (η^1-DPPM) reacts with $Mo(CO)_4(NBD)$ (NBD = bicyclo[2.2.1]heptadiene) to form $CpNi(\mu\text{-}CN)(\mu\text{-}DPPM)Mo(CO)_4$ (**2**)[7] suggesting that cyanide transfer to a low-valent metal might be less likely than the halide ligands in our previously studied systems. We report here on some chemistry of the 'metalloligand' CpNi(CN)(η^1-DPPM) together with the determination of the structure of **2**.

EXPERIMENTAL

All manipulations were carried out in an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were purified by standard methods and distilled under nitrogen prior to use. Literature methods were used to prepare CpNi(CN)(η^1-DPPM),[8] Pt(C_2H_4)(PPh_3)$_2$,[9] [RhCl(CO)$_2$]$_2$[10] and [IrCl(COD)]$_2$ (COD = cycloocta-1,5-diene).[11] Infrared spectra were obtained on a Mattson-Cygnus 100 Fourier transform spectrometer. Proton and $^{31}P\{^1H\}$ NMR spectra were recorded on an IBM/Bruker AF-200 instrument at 200.132 and 81.015 MHz respectively. Proton and phosphorus chemical shifts are referred, respectively to external tetramethylsilane (δ 0.0) and 85% phosphoric acid (δ 0.0) with positive shifts downfield of the reference. Microanalyses were by Galbraith Laboratories, Knoxville, TN.

Synthesis of Complexes

$$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}(C_6H_5)_2PCH_2P(C_6H_5)_2)Pt(CN)(P(C_6H_5)_3) \bullet CH_2Cl_2 \qquad (1)$$

To a mixture of 0.20 g (0.37 mmol) of CpNi(CN)(η^1-DPPM) and 0.28 g (0.37 mmol) of Pt(C_2H_4)(PPh_3)$_2$ was added 6 mL of dichloromethane whereupon effervescence occurred to give a dark, orange-brown solution. After stirring for 10 min at room temperature, the solution was filtered and the filtrate carefully layered with acetone and then hexane. After standing overnight, the product formed as brown, columnar crystals which were hand-separated from a small quantity of yellow plates following removal of the mother liquor with a syringe. *Anal. Calcd* for $C_{50}H_{44}NP_3Cl_2NiPt$ (%): C, 55.78; H, 4.13. Found: C, 55.2; H, 4.4. IR (Nujol mull): 2108(m) cm^{-1} ($\nu_{C\equiv N}$).[12] ^1H NMR (CD_2Cl_2): δ 6.78 – 7.73 (m, 35 H, C_6H_5), 4.90 (s, 5 H, C_5H_5), 4.38 (m, 2 H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta(P_A)$ 19.8 (dd, $J(P_A\text{-}P_B)$ = 67.3, $J(P_A\text{-}P_C)$ = 76.1, $^2J(Pt\text{-}P_A)$ = 409 Hz); $\delta(P_B)$ –2.8 (dd, $J(P_B\text{-}P_A)$ = 67.3, $J(P_B\text{-}P_C)$ = 14.9, $^1J(Pt\text{-}P_B)$ = 3100 Hz); $\delta(P_C)$ 7.3 (dd, $J(P_C\text{-}P_B)$ =14.9, $J(P_C\text{-}P_A)$ = 76.1, 1J(Pt-P_C) = 1715 Hz).[13]

$$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}CN)(\mu\text{-}(C_6H_5)_2PCH_2P(C_6H_5)_2)Mo(CO)_4 \qquad (2)$$

This complex was prepared by a modification of the published method[7] by dissolving CpNi(CN)(DPPM) in a mixture of THF and diethyl ether followed by addition of an equimolar quantity of solid $Mo(CO)_4(NBD)$. The solution turned dark red and was stirred for *ca.* 30 sec. On standing the product precipitated as dark red crystals which were briefly dried in vacuo following removal of the supernatant via syringe. The product was identified by its infrared spectrum which matched that reported previously.[7]

X-ray Crystallography

A dark, brown-orange, columnar crystal of **1** and a dark red, plate-shaped crystal of **2**, obtained as described above, were mounted on thin glass fibers with a thin coat of epoxy cement. General procedures for crystal orientation, unit cell determination and refinement and data collection on the CAD-4 diffractometer have been published.[14] Details specific to the present study appear in Table I. The monoclinic cell for **1** and the orthorhombic cell for **2** found by the CAD-4 software were confirmed by the observation of, respectively, *2/m* and *mmm* diffraction symmetry and the space groups were uniquely determined by the systematic absences observed in the final data sets. Data were collected in the quadrant h, k, $\pm l$ for **1** and in the octant h, k, l for **2**. Raw intensities were corrected for Lorentz and polarization effects, for a linear decline in the intensities of the check reflections (2.1% for **1**; 8.4% for **2**) and for absorption employing ψ scans for several reflections ($7.2 \leq \theta \leq 17.6$ for **1** and $5.4 \leq \theta \leq 8.0$ for **2**) with χ near 90°. The positions of the platinum atom in **1** and the molybdenum atom in **2** were obtained from origin-removed Patterson maps and the structures developed by successive cycles of full-matrix, least-squares refinement followed by the calculation of $\Delta\rho$ maps. In **1** it was soon evident that a molecule of solvent dichloromethane was also present and although the chlorine atoms appeared well-behaved, the carbon atom was disordered over several closely spaced sites. Two reasonable locations were deduced from careful consideration of a $\Delta\rho$ map and the known geometry of the molecule. These were input as fixed contributions with occupancies of 0.5 each and while some residual electron density remained in the region, no better model could be devised. In the final stages of the refinement, reasonable positions for most hydrogen atoms appeared in $\Delta\rho$ maps. These were included as fixed contributions (C-H = 0.95 Å) with isotropic displacement parameters 1.2 times those of the attached carbon atoms and updated periodically. Hydrogen atom numbers correspond to those of the attached carbon atoms. As a check on the correctness of the model for the cyano ligand in **2** (*i.e.*, $Ni - C{\equiv}N \rightarrow Mo$), refinement was also carried out with the identities of the carbon and nitrogen atoms interchanged. This led to unreasonable displacement parameters for the two atoms indicating the original choice to be correct. The neutral atom scattering factors used include corrections for the real and imaginary components of the effects of anomalous dispersion.[15] all calculations were performed on a VAX station 3100 computer with the **MolEN**[16] suite of programs. Final refined atomic coordinates for **1** and **2** are given in Tables II and III, respectively, while additional crystallographic data are provided as Supplementary Material.

TABLE I Summary of Crystallographic Data

	1	*2*
formula	$C_{50}H_{44}NP_3Cl_2NiPt$	$C_{35}H_{27}NO_4P_2NiMo$
fw	1076.54	742.21
cryst size, mm	0.33 × 0.53 × 0.60	0.05 × 0.13 × 0.30
cryst system	Monoclinic	Orthorhombic
space group	$P2_1/c$	Pbca
a, Å	14.182(2)	19.762(2)
b, Å	21.662(2)	21.263(4)
c, Å	15.125(1)	15.422(3)
β, deg	105.29(1)	
V, Å^3	4482(2)	6480(3)
Z	4	8
ρ_{calc}, g cm^{-3}	1.60	1.52
μ, cm^{-1}	38.3	11.0
range trans factors	0.7137 – 0.9998	0.8988 – 0.9988
temp, K	293	293
radtn	Mo Kα (Graphite monochromated, l = 0.71073 Å)	
scan type	ω/2θ	ω/2θ
scan range, deg	0.80 + 0.20(tan θ)	0.80 + 0.35(tan θ)
2Θ range, deg	2.0 – 46.0	2.0 – 44.0
total no. of refls	6735	3969
no. of unique refls	6230	3969
R_{int}	0.02	
no. obs data	4925($I \geq 3\sigma(I)$)	1901($I \geq 2\sigma(I)$)
no. parameters	514	272
$(\Delta/\sigma)_{max}$ in last cycle	0.05	0.05
R[a]	0.034	0.054
R_w[b]	0.047	0.050
GOF[c]	1.57	1.35
Δρ in final ΔF map, e/Å^3	1.56 to –0.18	0.55 to –0.26

[a] $R = [\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma\omega(||F_o|-|F_c||)^2/\Sigma\omega(|F_o|)^2]^{1/2}$ with $\omega = 1/(\sigma_F)^2$; $\sigma_F = \sigma(F^2)/2F$: $\sigma(F^2) = [(\sigma_I)^2+(0.04F^2)^2]^{1/2}$.

[c] $GOF = [\Sigma\omega(||F_o|-|F_c||)^2/(N_o - N_v)]^{1/2}$

where N_o and N_v are, respectively, the number of observations and variables.

TABLE II Positional Parameters (esd) for CpNi (μ-DPPM) Pt (CN) $(PPh_3) \cdot CH_2Cl_2$ (1)

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
Pt	0.17737(2)	0.22520(1)	0.31687(1)	2.278(5)
Ni	0.09633(5)	0.32555(4)	0.34238(5)	2.76(2)
P(1)	0.1886(1)	0.32247(8)	0.4746(1)	2.66(3)
P(2)	0.1266(1)	0.19404(8)	0.4400(1)	2.48(3)
P(3)	0.2493(1)	0.13408(8)	0.2858(1)	2.68(3)
N	0.2399(5)	0.3048(4)	0.1682(4)	6.7(2)
C(1)	0.2149(5)	0.2758(3)	0.2210(4)	3.6(1)
C(2)	0.1716(5)	0.2505(3)	0.5303(4)	3.4(1)

TABLE II (*Continued*)

Atom	*x*	*y*	*z*	$B_{eq}(Å^2)$
C(3)	0.1671(5)	0.3803(3)	0.5568(4)	3.3(1)
C(4)	0.0755(6)	0.3833(4)	0.5718(5)	5.4(2)
C(5)	0.0541(6)	0.4249(5)	0.6327(5)	6.2(2)
C(6)	0.1233(6)	0.4645(4)	0.6782(5)	5.1(2)
C(7)	0.2148(6)	0.4630(4)	0.6652(5)	4.8(2)
C(8)	0.2384(5)	0.4198(3)	0.6049(5)	3.9(2)
C(9)	0.3185(5)	0.3307(3)	0.4862(4)	3.1(1)
C(10)	0.3912(5)	0.3096(4)	0.5626(5)	4.2(2)
C(11)	0.4875(6)	0.3199(4)	0.5705(6)	5.1(2)
C(12)	0.5151(6)	0.3538(5)	0.5050(6)	6.5(2)
C(13)	0.4456(6)	0.3764(5)	0.4300(6)	6.7(3)
C(14)	0.3475(5)	0.3642(4)	0.4203(5)	4.5(2)
C(15)	0.1695(4)	0.1222(3)	0.5013(4)	2.6(1)
C(16)	0.2666(5)	0.1157(3)	0.5486(4)	3.3(1)
C(17)	0.3005(5)	0.0626(4)	0.5969(5)	3.9(2)
C(18)	0.2391(5)	0.0157(3)	0.6000(5)	4.0(2)
C(19)	0.1407(5)	0.0202(3)	0.5525(5)	4.4(2)
C(20)	0.1062(5)	0.0732(4)	0.5046(5)	3.9(2)
C(21)	–0.0047(4)	0.1891(3)	0.4248(4)	2.9(1)
C(22)	–0.0661(5)	0.1811(4)	0.3373(4)	3.6(2)
C(23)	–0.1655(5)	0.1731(4)	0.3236(6)	5.2(2)
C(24)	–0.2049(5)	0.1747(4)	0.3976(6)	5.6(2)
C(25)	–0.1459(5)	0.1815(4)	0.4840(5)	4.8(2)
C(26)	–0.0477(5)	0.1895(4)	0.4982(5)	4.0(2)
C(27)	0.3768(4)	0.1266(3)	0.3538(4)	3.2(1)
C(28)	0.4176(5)	0.1729(4)	0.4137(4)	3.6(2)
C(29)	0.5131(5)	0.1694(4)	0.4664(5)	4.7(2)
C(30)	0.5679(5)	0.1173(5)	0.4609(6)	5.7(2)
C(31)	0.5297(6)	0.0716(4)	0.3992(6)	6.2(2)
C(32)	0.4345(5)	0.0767(4)	0.3450(5)	4.9(2)
C(33)	0.1848(4)	0.0647(3)	0.3057(4)	3.2(1)
C(34)	0.2294(6)	0.0125(4)	0.3534(5)	4.7(2)
C(35)	0.1742(7)	–0.0400(4)	0.3566(7)	6.2(2)
C(36)	0.0766(7)	–0.0401(4)	0.3162(7)	6.8(3)
C(37)	0.0325(6)	0.0107(4)	0.2708(6)	5.8(2)
C(38)	0.0869(5)	0.0627(4)	0.2661(5)	4.3(2)
C(39)	0.2608(4)	0.1171(3)	0.1696(4)	3.1(1)
C(40)	0.2379(6)	0.0605(4)	0.1284(5)	5.0(2)
C(41)	0.2493(7)	0.0489(4)	0.0432(5)	5.9(2)
C(42)	0.2864(6)	0.0930(5)	-0.0024(5)	5.7(2)
C(43)	0.3090(6)	0.1497(4)	0.0361(5)	4.9(2)
C(44)	0.2978(5)	0.1617(4)	0.1225(5)	4.2(2)
C(45)	0.0501(6)	0.4173(3)	0.3018(6)	5.5(2)
C(46)	–0.0238(6)	0.3858(4)	0.3314(5)	6.1(2)
C(47)	–0.0539(6)	0.3379(4)	0.2739(7)	6.4(2)
C(48)	0.0014(7)	0.3365(4)	0.2132(6)	6.3(2)
C(49)	0.0616(6)	0.3869(4)	0.2270(5)	6.0(2)
Cl(1s)	0.5511(3)	0.2205(2)	0.2366(3)	12.6(1)
Cl(2s)	0.6435(4)	0.3398(2)	0.2573(3)	14.9(2)
C(1s)	0.590(1)	0.2810(6)	0.3060(8)	11.0(4)*
C(1sa)	0.5249	0.2930	0.2649	11*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$Beq = (8\pi^2/3)\sum_i \sum_j U_{ij}a^{*}ia^{*}{}_j a_i \cdot a_j$$

TABLE III Positional Parameters (esd) for CpNi (μ – CN) (μ – DPPM) Mo $(CO)_4$ (2)

Atom	*x*	*y*	*z*	$B_{eq}(Å^2)$
Mo	0.12153(5)	0.10119(5)	0.14725(7)	3.04(2)
Ni	−0.00745(7)	0.16009(7)	0.4104(1)	3.32(3)
P(1)	0.1643(1)	0.0500(1)	0.2867(2)	2.77(7)
P(2)	0.0879(2)	0.1196(1)	0.4491(2)	2.81(7)
O(1)	0.0699(5)	0.1416(4)	−0.0361(6)	7.2(3)
O(2)	0.0420(4)	−0.0226(4)	0.0966(6)	6.3(2)
O(3)	0.2548(4)	0.0522(5)	0.0607(5)	6.1(2)
O(4)	0.1934(5)	0.2329(4)	0.1648(6)	6.8(3)
N	0.0404(5)	0.1351(5)	0.2290(6)	4.8(3)
C(1)	0.0880(6)	0.1297(6)	0.0342(8)	5.0(3)
C(2)	0.0711(6)	0.0211(6)	0.1185(7)	4.4(3)
C(3)	0.2038(5)	0.0701(5)	0.0924(8)	3.9(3)
C(4)	0.1688(6)	0.1852(5)	0.1589(8)	3.9(3)
C(5)	0.0171(5)	0.1474(5)	0.2949(8)	3.9(3)
C(6)	−0.0603(6)	0.2443(6)	0.4367(9)	5.9(4)
C(7)	−0.0376(7)	0.2208(6)	0.5098(9)	6.4(4)
C(8)	−0.0665(6)	0.1615(7)	0.5197(9)	6.5(4)
C(9)	−0.1094(6)	0.1480(6)	0.452(1)	7.8(5)
C(10)	−0.1024(5)	0.1998(6)	0.3972(9)	5.7(3)
C(11)	0.1692(5)	−0.0350(5)	0.2680(7)	2.5(2)*
C(12)	0.1141(5)	−0.0744(5)	0.2766(7)	3.5(2)*
C(13)	0.1172(6)	−0.1376(6)	0.2551(9)	5.2(3)*
C(14)	0.1759(6)	−0.1620(6)	0.2248(8)	4.8(3)*
C(15)	0.2292(6)	−0.1243(6)	0.2130(8)	5.2(3)*
C(16)	0.2286(5)	−0.0612(5)	0.2333(7)	3.6(3)*
C(17)	0.2498(5)	0.0655(5)	0.3249(7)	3.1(2)*
C(18)	0.2875(5)	0.1131(5)	0.2907(7)	3.6(3)*
C(19)	0.3552(6)	0.1242(6)	0.3214(8)	4.6(3)*
C(20)	0.3807(6)	0.0870(5)	0.3829(7)	4.1(3)*
C(21)	0.3447(6)	0.0382(6)	0.4178(9)	5.1(3)*
C(22)	0.2780(6)	0.0282(5)	0.3890(8)	4.1(3)*
C(23)	0.1579(5)	0.1735(5)	0.4435(7)	2.8(2)*
C(24)	0.1515(6)	0.2290(6)	0.3977(8)	4.6(3)*
C(25)	0.2049(7)	0.2718(7)	0.395(1)	6.6(4)*
C(26)	0.2627(7)	0.2563(7)	0.4371(9)	6.2(4)*
C(27)	0.2722(6)	0.2040(6)	0.4840(9)	5.3(3)*
C(28)	0.2177(6)	0.1601(5)	0.4882(8)	4.0(3)*
C(29)	0.0865(5)	0.0938(5)	0.5613(7)	3.0(2)*
C(30)	0.0898(6)	0.1399(5)	0.6267(7)	3.9(3)*
C(31)	0.0835(6)	0.1209(6)	0.7147(8)	4.5(3)*
C(32)	0.0756(6)	0.0613(6)	0.7349(8)	4.5(3)*
C(33)	0.0719(6)	0.0158(6)	0.6740(8)	4.7(3)*
C(34)	0.0757(5)	0.0327(5)	0.5867(8)	3.7(3)*
C(35)	0.1139(5)	0.0483(5)	0.3895(6)	2.3(2)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$Beq = (8\pi^2/3)\sum_i\sum_j U_{ij}a^{*}ia^{*}{}_{j}a_i \cdot a_j$$

RESULTS AND DISCUSSION

Synthesis of Complexes

Reaction of CpNi(CN)(η^1-DPPM) with Pt(C_2H_4)(PPh_3)$_2$ occurs readily to give a brown-orange, crystalline product analyzing as CpNiPt (DPPM)(CN)(PPh_3) · CH_2Cl_2 (**1**). The structure shown has been established by x-ray crystallography and the spectroscopic data are consistent with this formulation. Thus the $^{31}P\{^1H\}$ NMR spectrum consists of three doublet of doublet resonances of equal intensity, all possessing ^{195}Pt satellites. That at δ 19.8 with J(Pt-P) = 409 Hz can be assigned to DPPM coordinated to nickel with the small value for the Pt-P coupling consistent with a two-bond coupling, presumably through the Pt-Ni bond. The assignment of the δ 7.3 resonance (J(Pt-P) = 1715 Hz) to the triphenylphosphine ligand, which lies *trans* to the Pt-Ni bond, is based on the spectrum reported for [Ni(MeCN)$_2$(μ-DPPM)Pt(η_2-DPPM)](BF_4)$_2$ where J(Pt-P) for the phosphorus *trans* to the Pt-Ni bond is 1123 Hz while J(Pt-P) for the phosphorus atoms *cis* to this bond is more than twice as large.[17] Consistent with this is the assignment of the δ -2.8 resonance (J(Pt-P) = 3100 Hz) to DPPM coordinated to platinum. The proton NMR spectrum shows the DPPM methylene protons to be equivalent. Since the structure in the solid state (Figure 1) suggests that they are in different environments, this observation suggests the molecule is fluxional *via* a twisting motion about the metal-metal bond.

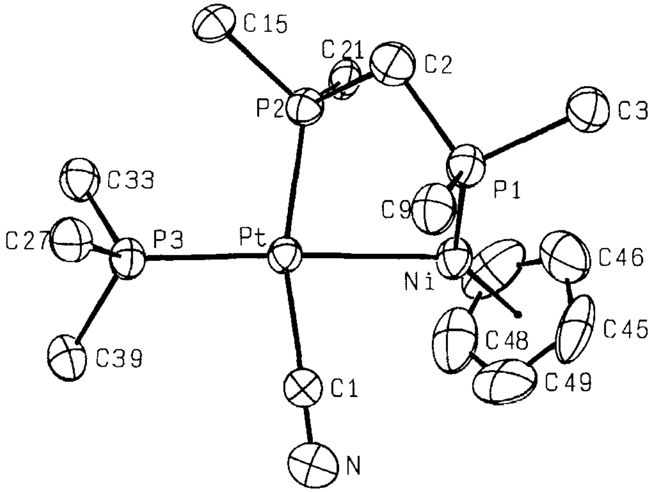
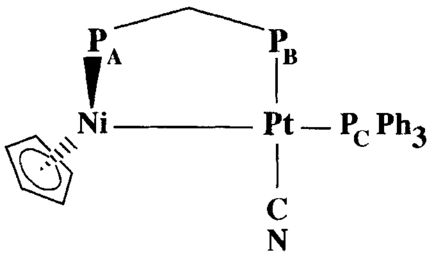


FIGURE 1 A perspective view of CpNi(μ-DPPM)Pt(CN)(PPh_3) (**1**). Thermal ellipsoids are drawn at the 40% probability level. Only the *ipso* carbons of the phenyl rings are shown and the hydrogen atoms are omitted for clarity.



1

As shown by the structure determination, the cyano ligand has transferred from nickel to platinum in the formation of **1**. With the resulting increase in the formal oxidation state of platinum, the reactivity of **1** is therefore disappointingly low as we have found previously with related heterobimetallic complexes. While it did apparently react with an excess of dimethylacetylene dicarboxylate at room temperature, the phosphorus NMR of the resulting mixture was exceedingly complex suggesting several products had formed and no characterizable material could be isolated despite considerable effort. Also, despite the clean formation of **1** and **2** from CpNi(CN)(η^1-DPPM) and the indicated Pt(0) and Mo(0) precursors, little success was had in using the 'metalloligand' to generate other heterobimetallics. Thus with $[RhCl(CO)_2]_2$ or with $[IrCl(COD)]_2$ plus one equivalent of triphenylphosphine, for example, only ill-defined solids were obtained.

Description of Structures

The structure of 1 consists of molecules of CpNi(μ-DPPM)Pt(CN)(PPh_3) interspersed with molecules of solvent dichloromethane. There are no unusually short intermolecular contacts. A perspective view of the inner core is shown in Figure 1 while pertinent bond distances and interbond angles are presented in Table IV. As is evident from Figure 1, the coordination about platinum is only approximately square planar. The distortions from ideal geometry include a bending of P(2) and C(1) towards the nickel atom and, particularly, a significant displacement of the cyano ligand out of the mean plane defined by Pt, Ni, P(2) and P(3). This is likely due to relief of short intramolecular contacts as an ortho hydrogen on the phenyl ring built on C(39) is only 2.54 and 2.58 Å, respectively, from N and C(1). There is a significant twist in the molecule about the Ni—Pt axis as evidenced by the P(2)—Pt—Ni—P(1) torsion angle of 56.06°. This presumably occurs to minimize contacts between the phenyl groups on P(2) and those on P(3). A notable feature of **1** is the short Pt—Ni distance of 2.5356(9) Å. This is

TABLE IV Bond Distances (Å) and Interbond Angles (°) for CpNi(μ-DPPM)Pt(CN)(PPh_3) · CH_2Cl_2 (1)

Pt—Ni	2.5356(9)	Ni—C(45)	2.132(8)
Pt—P(2)	2.269(2)	Ni—C(46)	2.118(8)
Pt—P(3)	2.326(2)	Ni—C(47)	2.125(9)
Pt—C(1)	1.998(7)	Ni—C(48)	2.073(9)
Ni—P(1)	2.082(2)	Ni—C(49)	2.146(8)
Ni—Pt—P(2)	82.85(5)	P(3)—Pt—C(1)	95.9(2)
Ni—Pt—P(3)	177.19(4)	Pt—Ni—P(1)	85.61(6)
Ni—Pt—C(1)	81.9(2)	Pt—Ni—C′	132.8(3)[a]
P(2) —Pt—P(3)	99.48(6)	P(1) —Ni—C′	141.4(4)[a]
P(2) —Pt—C(1)	164.0(2)	Pt—C(1) —N	177.4(8)

[a] C′ is the centroid of the cyclopentadienyl ring.

significantly shorter than the value of 2.5892(9) Å found in [Ni(CNMe)(μ-CNMe)(μ-DPPM)$_2$PtCl]Cl[18] and much shorter than that of 2.689(2) Å found in NiCl(μ-CO)(μ-DPPM)$_2$PtCl,[19] the only other two heterobimetallic Pt/Ni complexes that have been structurally characterized. It is possible that the smaller number of bridging ligands present in **1** allows for a stronger metal-metal interaction but it may also be that there is a highly directional σ-bond between the metal atoms. We thank a referee for the latter suggestion.

The crystal structure of **2** consists of the packing of CpNi(μ-CN)(μ-DPPM)Mo(CO)$_4$ molecules with the shortest intermolecular contacts being those of O(3) with a cyclopentadienyl hydrogen (H(9) at – ½ +x, y, – ½ – z, 2.49 Å) and with a phenyl hydrogen (H(22) at ½ – x, –y, – ½ +z, 2.48 Å). A perspective view of the core is shown in Figure 2 while pertinent bond distances and interbond angles are given in Table V. The structure confirms the original suggestion based on limited spectroscopic data that the cyano ligand bridges the two metals and that it is only N-bonded to molybdenum. The intermetallic distance of 4.953(1) Å is clearly too long for a direct interaction to occur. The {Ni-CN} unit deviates only slightly from linearity while the {Mo-NC} unit is distinctly non-linear. This is likely due to the constraints of the bridging DPPM ligand although similar M-N-C angles have also been found in $(NH_3)_5Co(\mu\text{-}NC)Co(CN)_5 \cdot H_2O$[20] and [CpRu(dppe)(μ-CN)Ru(PPh_3)$_2$Cp]PF_6 (dppe = 1,2-bis(diphenylphosphino)ethane)[21] where no other bridging ligands are present. The Mo-N distance is comparable to the Ru-N distance in the latter complex. The geometry about molybdenum is approximately octahedral while that about nickel is comparable to that found in **1**.

TABLE V Bond Distances (Å) and Interbond Angles (°) for CpNi(μ-CN)(μ-DPPM)Mo(CO)$_4$ (2)

Mo—P(1)	2.554(3)	Ni—C(5)	1.86(2)
Mo—N	2.16(1)	Ni—C(6)	2.11(1)
Mo—C(1)	1.96(2)	Ni—C(7)	2.09(2)

TABLE V (*Continued*)

Mo — C(2)	2.02(2)	Ni — C(8)	2.05(1)
Mo — C(3)	1.95(1)	Ni — C(9)	2.13(2)
Mo — C(4)	2.02(1)	Ni — C(10)	2.07(1)
Ni — P(2)	2.155(3)	N — C(5)	1.15(1)
P(1) — Mo — N	84.0(3)	C(2) — Mo — C(3)	91.7(5)
Π(1) — Mo — C(1)	172.8(4)	C(2) — Mo — C(4)	171.9(5)
P(1) — Mo — C(2)	89.4(4)	C(3) — Mo — C(4)	87.3(5)
P(1) — Mo — C(3)	86.9(4)	P(2) — Ni — C(5)	88.8(4)
P(1) — Mo — C(4)	98.6(4)	P(2) — Ni — C′	135.8(4)[a]
N — Mo — C(1)	99.5(5)	C(5) — Ni — C′	135.2(4)[a]
N — Mo — C(2)	92.5(5)	Mo — N — C(5)	153(1)
N — Mo — C(3)	169.9(5)	Mo — C(1) — O(1)	174(1)
N — Mo — C(4)	89.8(5)	Mo — C(2) — O(2)	175(1)
C(1) — Mo — C(2)	84.2(6)	Mo — C(3) — O(3)	178(1)
C(1) — Mo — C(3)	90.0(6)	Mo — C(4) — O(4)	178(1)
C(1) — Mo — C(4)	87.8(5)	Ni — C(5) — N	170(1)

[a] C′ is the centroid of the cyclopentadienyl ring.

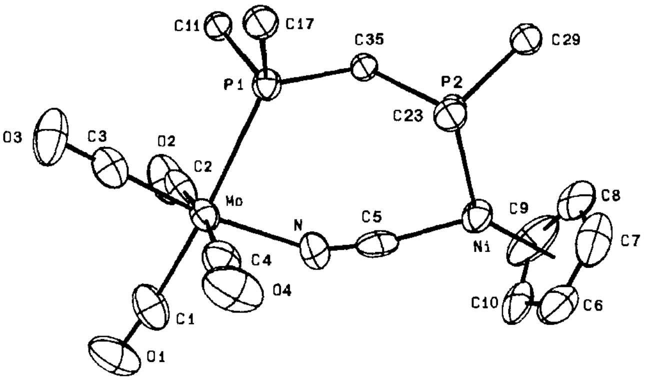


FIGURE 2 A perspective view of CpNi(μ-CN)(μ-DPPM)Mo(CO)$_4$ (2). Thermal ellipsoids are drawn at the 40% probability level. Only the ipso carbons of the phenyl rings are shown and the hydrogen atoms are omitted for clarity.

Acknowledgments

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[12] Key to infrared band intensities: m, medium.

[13] Key to NMR peak multiplicities: s, singlet; dd, doublet of doublets; m, multiplet.

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