Organometallics **1988,** *7,* 871-878

Reactions of Isocyanides with the Unsaturated Triosmium–Platinum Cluster Complex $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$. X-ray Crystal Structures of $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CyNC)$ and $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CyNC)$

Paul Ewing and Louis J. Farrugia*

Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, Scotland, U.K.

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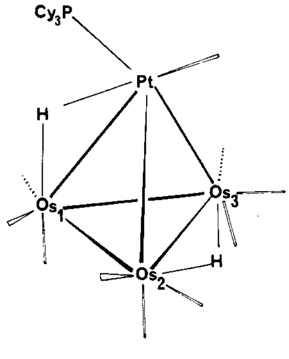
Treatment of $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ (1) with RNC affords the 60-electron butterfly adducts $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)(RNC)$ (**2a**, R = Cy; **2b**, R = *t*-Bu). ^1H and ^{13}C NMR studies show that addition of RNC at 195 K yields principally one isomer, which has the isocyanide ligand bonded to an osmium center. Reaction at 273 K produces three isomers in thermodynamic equilibrium. Reflux of hexane solutions of **2** results in facile decarbonylation, affording in high yields the 58-electron unsaturated complexes $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(RNC)$ (**3a**, R = Cy; **3b**, R = *t*-Bu). Crystal data for **3a**: triclinic, space group $P\bar{1}$, $a = 11.283$ (3) Å, $b = 11.697$ (5) Å, $c = 16.367$ (8) Å, $\alpha = 89.23$ (4)°, $\beta = 74.79$ (3)°, $\gamma = 76.94$ (3)°, $V = 2028$ (1) Å^3, $Z = 2$, final R (R_w) values of 0.055 (0.053) for 4055 independent observed data ($I > 2.5\sigma(I)$). **3a** has a closo tetrahedral metal core with the hydrido ligands bridging the Os(2)–Os(3) edge (2.752 (1) Å) and the Pt–Os(1) vector (2.844 (1) Å). The remaining two Os–Os edges are almost equal in length (Os(1)–Os(2) = 2.745 (1) Å; Os(1)–Os(3) = 2.742 (1) Å), while the other Pt–Os edges differ slightly (Pt–Os(2) = 2.773 (1) Å; Pt–Os(3) = 2.781 (1) Å). The isocyanide ligand is bonded to the platinum atom. Treatment of **3a** with CH_2N_2 affords the 60-electron methylene adduct $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CyNC)$ (**4**). Crystal data for **4**: triclinic, space group $P\bar{1}$, $a = 12.189$ (3) Å, $b = 13.180$ (4) Å, $c = 16.901$ (6) Å, $\alpha = 108.31$ (4)°, $\beta = 90.62$ (4)°, $\gamma = 114.20$ (2)°, $V = 2320$ (1) Å^3, $Z = 2$, final R (R_w) = 0.059 (0.080) for 6659 independent observed reflections ($I > 2.5\sigma(I)$). The tetrahedral Os_3Pt framework has a methylene-bridged Os–Os vector (Os(2)–Os(3) = 2.841 (2) Å) and hydrides spanning an Os–Os bond (Os(1)–Os(2) = 2.965 (2) Å) and an Os–Pt bond (Os(1)–Pt = 2.865 (1) Å), with remaining metal–metal separations Os(1)–Os(3) = 2.796 (2) Å, Pt–Os(2) = 2.858 (1) Å, and Pt–Os(3) = 2.787 (2) Å. Complexes **3** and **4** readily protonate along Os–Os edges on treatment with CF_3COOH or HBF_4.

Introduction

Transition-metal cluster compounds containing isocyanide ligands[1] are still relatively rare. As well as the normal η^1 terminal bonding mode, these ligands also show a propensity for μ_n-η^2 C–N bridged bonding in polynuclear complexes. Examples include μ_2-η^2 bonding in $Ni_4(t\text{-}BuNC)_7$,[2] μ_3-η^2 bonding in $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$,[3] and $Os_6(CO)_{18}(4\text{-}MeC_6H_4NC)_2$,[4] and μ_4-η^2 bonding in $Ru_5(CO)_{14}(t\text{-}BuNC)_2$.[5] In this latter complex the μ_4-η^2-isocyanide C–N bond length is 1.375 (8) Å and exemplifies the "activation" of an unsaturated organic ligand by multisite coordination to a transition-metal cluster core.[6] The well-known reactivity of isocyanide ligands toward insertion into transition-metal–alkyl and –hydride bonds[1] is illustrated in the cluster context by the work of Adams and Golembeski[7-9] on reactions of isocyanides with the unsaturated hydrido–carbonyl complex $Os_3(\mu\text{-}H)_2(CO)_{10}$. Initial treatment with RNC leads to the 48-electron adducts $Os_3(\mu\text{-}H)(H)(CO)_{10}(RNC)$ (R = Me, Ph, *t*-Bu), and these then readily lose CO on thermolysis, giving the unsaturated nonacarbonyl derivatives.[7,8] Depending on solvent polarity further thermolysis yields compounds containing either an μ_2-η^2-formimidoyl ligand (μ_2-η^2-HC═NR)[8] or an μ_2-η^1-iminyl or -amido–carbene (μ-C═N(H)R) group,[8,9] resulting from insertion into Os—H bonds.



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It has been previously shown that the unsaturated hydrido–carbonyl complex $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ (1)[10] readily reacts with a variety of two-electron donor ligands

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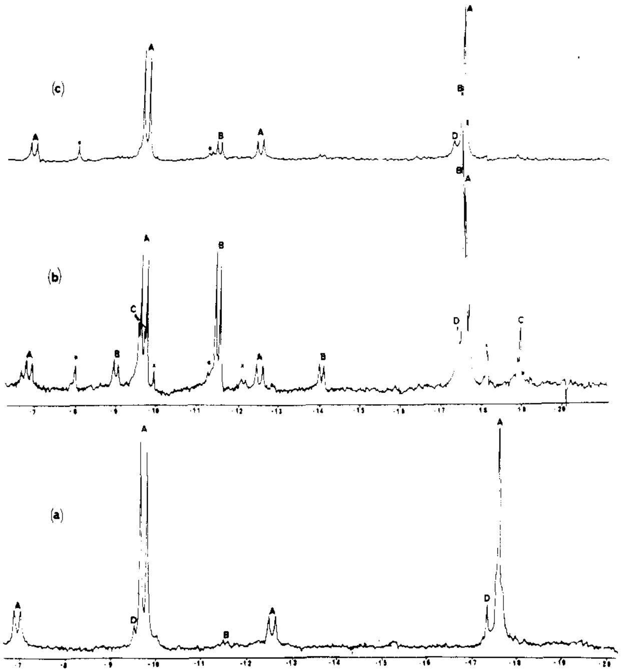

Figure 1. ^1H NMR spectra (233 K) in the hydride region of complex 1: (a) immediately after addition of 1 mol equiv of CyNC at 195 K; (b) as for (a) but addition at 273 K; (c) same solution as (b) after warming to ambient temperature for 1 h. The asterisk (*) denotes signals from **3a**; the x denotes minor uncharacterized species.

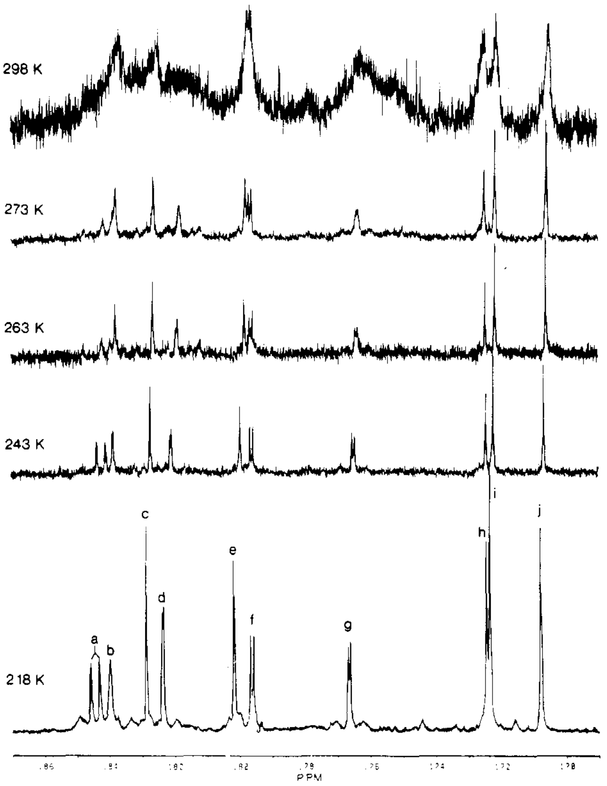

Figure 2. Variable-temperature $^{13}C\{^1H\}$ NMR spectrum of $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)(CyNC)$ (**2a**) (isomer A). See Table I for assignments.

giving 60-electron adducts containing either a tetrahedral[11] or a butterfly[11,12] Os_3Pt core. We therefore investigated the reactions of 1 with isocyanide ligands in the hope of synthesizing cluster compounds containing multisite-bound RNC-derived groups. While we found no evidence for such moieties, a facile isocyanide transfer between Os and Pt centers is implicated by the reaction sequences described below.

Results and Discussion

Treatment of solutions of $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ (1) with RNC (R = Cy, *t*-Bu) results in rapid discharge of the dark green color of 1, giving the orange-yellow adducts $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)(L)$ (**2a**, L = CyNC; **2b**, L = *t*-BuNC). ^1H NMR studies show that several isomers of 2 are formed depending on the reaction temperature. Addition of RNC at 195 K results in the formation of mainly one isomer (isomer A). Figure 1a shows the ^1H NMR spectrum in the hydride region, recorded at 233 K, of the reaction mixture formed by addition of 1 mol equiv of CyNC to a solution of 1 at 195 K. Isomer A shows signals due to $Os(\mu\text{-}H)Pt$ and $Os(\mu\text{-}H)Os$ protons at −9.78 and −17.63 ppm, respectively, for L = CyNC. Traces of isomer B, and signals attributed to a third uncharacterized species D, are also detectable. These latter unidentified signals appear reproducibly in all the spectra we have recorded and do not appear to change significantly in intensity with time.

Addition of CyNC to 1 at 273 K (Figure 1b) gives rise to three principal species. As well as signals due to A, resonances arising from the isomers B [$Os(\mu\text{-}H)Pt$ −11.59 ppm, $J(Pt\text{-}H)$ = 503, $J(P\text{-}H)$ = 11 Hz; $Os(\mu\text{-}H)Os$ −17.56 ppm, $J(Pt\text{-}H)$ = 26, $J(P\text{-}H)$ = 1.5 Hz] and C [$Os(\mu\text{-}H)Pt$ −9.70 ppm, $J(Pt\text{-}H)$ = 570, $J(P\text{-}H)$ = 15 Hz; $Os(\mu\text{-}H)Os$ −18.94 ppm, $J(Pt\text{-}H)$ = 16 Hz] are also visible. Warming this solution to ambient temperatures for 1 h gives the spectrum shown in Figure 1c, where the signals due to C have disappeared and those from B are diminished greatly in intensity. Warming under similar conditions a sample initially prepared at 195 K gives rise to a spectrum closely resembling that in Figure 1c. It thus seems likely that the species A, B, and C are structural isomers of **2a** and **2b**, which are in thermodynamic equilibrium. The relative proportions of isomers A, B, and C varied from sample to sample, consistent with the view that B and C are formed under kinetic control. The difficulty of controlling the exact mixing temperature and time of reaction accounts for these varying proportions. Signals from C disappear rapidly (ca. 5 min at 298 K), while the equilibrium between A and B is established more slowly.

The variable-temperature ^{13}C NMR spectrum of isomer A in the carbonyl region is shown in Figure 2, with parameters given in Table I. The large ^{195}Pt coupling on resonance f clearly indicates this is due to a carbonyl directly bonded to Pt. It is assumed that isomers A–C have similar butterfly structures to the crystallographically characterized adducts **2c** (R = Cy, L = CO)[11] and **2d** (R = Ph, L = PPh_3).[12] From the magnitudes of ^{195}Pt couplings (Table I) it is apparent that the phosphine ligand and one hydride remain bonded to Pt. The isocyanide must therefore be coordinated to an Os center. A broad signal for this ligand is seen at 110.8 ppm. Carbonyl assignments in Table I are based on selective ^1H decoupling and by comparison with NMR data for the related adducts $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)(L)$ (L = CO and PCy_3).[13] Although the detailed structure of isomer A is not unam-

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Table I. NMR Parameters for $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)(CyNC)$ (2a) (Isomer A)

^{13}C Data[a]

reson[b]	chem shift/ppm	mult[c]	assign	J/Hz[d] Pt–C	P–C	H1–C	H2–C
a	184.4	d	C6		13.3		w
b	184.0	s	C3			10.4	
c	182.9	s	C2/C4			3.9	
d	182.3	d	C7		1.2		4.3
e	180.2	s	C2/C4	18		2.3	
f	179.6	d	C1	1784	4.6	28.7	
g	176.7	d	C5	42	3.2		6.7
h	172.5	s	C10/C8				
i	172.4	s	C9				8.8
j	170.8	s	C10/C8				3.4
	110.8	s	CyNC				

^{1}H Data[e]

−9.78 (d, Os(μ-H)Pt, J(Pt–H) = 565, J(P–H) = 14.2 Hz)

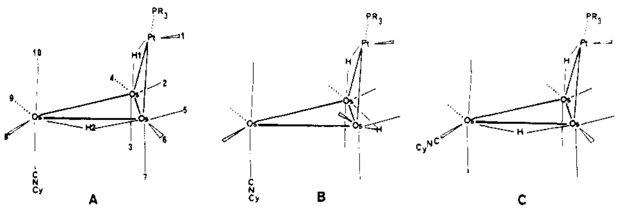
−17.63 (d, Os(μ-H)Os, J(Pt–H) = 32, J(P–H) = 1.2 Hz)

^{31}P Data[f]

51.6 (s, PtP, J(Pt–P) = 2520 Hz)

[a] 218 K, CD_2Cl_2/CH_2Cl_2, 1:1. [b] Figure 2. [c] Multiplicities based on ^{1}H decoupled spectra. [d] w indicates small unresolved coupling. [e] 233 K, $CDCl_3$, ppm relative to TMS. [f] 233 K, $CDCl_3$, ppm relative to external H_3PO_4.

Chart I



biguously determined by the spectroscopic data, several points are clear: (a) the two hydride ligands are not proximate since no carbonyl shows coupling to more than one hydride; (b) since three Os-bound carbonyls show couplings to H1, the isocyanide is not bonded to the Os atom involved in the Os(μ-H)Pt bridge; (c) on warming above 218 K the three resonances, a, d, and g broaden more rapidly than the others, consistent with their assignment as the carbonyls C6, C7, and C5, respectively, of an $Os(CO)_3$ group undergoing a tripodal rotation; (d) the broad stretch at 2175 cm^{-1} in the solid-state IR spectrum indicates a terminal CyNC ligand. The structure shown for A is consistent with these data (Chart I).

The variable-temperature ^{13}C NMR spectrum of A clearly shows further exchange processes are occurring at 298 K, but inherent instability prevents a detailed examination of this fluxional behavior. The structures of B and C shown are tentative and are based on the ^{1}H NMR data. The shifts and coupling constants involving the hydride ligands in B are extremely similar to those found in the complex 2c[13] and suggest that B has an analogous structure with proximate hydrides. NMR parameters for C more closely resemble those of A, and the facile conversion of C to A may occur via a trigonal twist mechanism involving an $Os(CO)_3(RNC)$ group.

Isocyanides show a propensity for axial substitution in derivatives of $M_3(CO)_{12}$ (M = Ru,[14] and Os[15]), whereas in corresponding phosphine complexes exclusive equatorial substitution is found.[16] In the complexes $Os_3(\mu\text{-}H)(H)(CO)_{10}(L)$, for example, with L = t-BuNC axial coordination is observed,[7,8] while for L = PPh_3 the bulky phosphine occupies an equatorial site.[17] There is, however, NMR evidence for equatorial/axial isomerization in $Os_3(CO)_{11}(t\text{-BuNC})$,[15] and X-ray analysis shows the t-BuNC ligand in $Os_3(\mu\text{-}H)_2(CO)_9(t\text{-BuNC})$ occupies an equatorial site.[7,8] It seems likely that although electronic factors favor axial coordination of RNC groups, steric constraints may result in equatorial ligation. The exact coordination site of the RNC ligand in the isomers of **2a,b** is thus unclear. Unfortunately despite many attempts no crystals suitable for X-ray diffraction could be obtained.

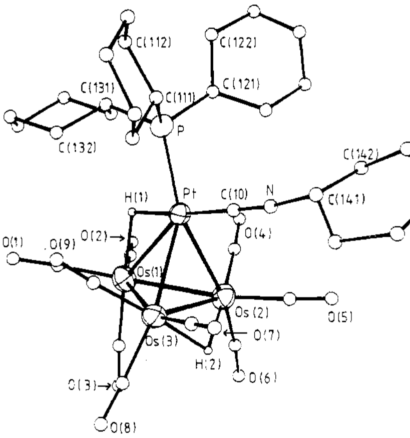


Figure 3. Molecular geometry and atomic labeling scheme for $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CyNC)$ (**3a**).

Solutions of the isomers of **2a,b** readily lose CO, and reflux in hexane for ca. 1 h under dinitrogen purge results in high yields of the dark green crystalline complexes $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(RNC)$ (**3a**, R = Cy; **3b**, R = t-Bu). Solution IR spectra indicated terminal RNC and CO ligands, while ^{1}H and ^{13}C NMR data suggested a structure similar to the parent unsaturated complex **1** with one CO substituted by an isocyanide ligand. Thus for **3a** hydride resonances are observed at −8.01 and −11.35 ppm due to Os(μ-H)Os and Os(μ-H)Pt moieties, respectively. The shift to high frequency for the Os(μ-H)Os proton is characteristic of unsaturated systems[10,13] and compares with a value of −17.63 ppm observed for isomer A of **2a** for the same unit. The ^{13}C NMR spectrum of **3a** in the carbonyl region shows five resonances (ratio 2:2:2:1:2) and is very similar to that of **1**[13] except that no signal shows a large ^{195}Pt coupling; i.e., there is no CO ligand directly bonded to Pt. The CyNC carbon occurs at 115.3 ppm as a broad weak resonance without detectable ^{195}Pt coupling. For verification of the structure of complexes **3**, a single-crystal X-ray diffraction study of **3a** was undertaken. Figure 3 shows the molecular structure and crystallographic labeling, with a stereoview illustrated in Figure 4 (supplementary material). Atomic coordinates and important metrical parameters are given in Tables II and III, respectively. A nearly linear (C(10)–N–C(141) = 166 (3)°) isocyanide group is ligated to the Pt atom and lies over the Pt–Os(2)–Os(3) face. The structure of **3a** is thus related to that of **1**[10] by replacement of the CO ligand on the Pt atom by a CyNC group. Metal–metal separations parallel those found in **1**, and these are quoted for convenience in Table III. Apart from the Pt–Os(3) separation, these distances differ by only 0.02–0.04 Å in the two complexes. The metal framework in **3a** is essentially tetra-

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Table II. Final Positional Parameters (Fractional Coordinates) with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters (U_{eq}, Å^2) for $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CNCy)$ (3a)[a]

	x/a	y/b	z/c	U_{eq}
Os(1)	0.23121 (8)	−0.26433 (9)	0.24738 (6)	0.052
Os(2)	0.14867 (8)	−0.08184 (8)	0.15372 (6)	0.048
Os(3)	0.08043 (8)	−0.05778 (8)	0.32795 (6)	0.049
Pt	−0.02716 (7)	−0.19810 (7)	0.24690 (5)	0.033
P	−0.1508 (4)	−0.3372 (4)	0.2591 (3)	0.036
N	−0.241 (2)	0.002 (2)	0.238 (1)	0.094
O(1)	0.2557 (18)	−0.4250 (17)	0.3919 (13)	0.134
O(2)	0.3741 (18)	−0.4445 (18)	0.1062 (15)	0.115
O(3)	0.4497 (15)	−0.1522 (18)	0.2425 (13)	0.129
O(4)	0.1705 (19)	−0.2683 (19)	0.0198 (12)	0.110
O(5)	−0.0158 (19)	0.1171 (17)	0.0872 (14)	0.126
O(6)	0.398 (2)	−0.029 (2)	0.060 (1)	0.170
O(7)	−0.1417 (18)	0.1503 (18)	0.3845 (14)	0.113
O(8)	0.2532 (19)	0.0263 (19)	0.4138 (15)	0.149
O(9)	−0.005 (2)	−0.207 (2)	0.471 (1)	0.115
C(1)	0.243 (2)	−0.362 (2)	0.335 (2)	0.079
C(2)	0.318 (2)	−0.373 (2)	0.159 (2)	0.089
C(3)	0.365 (2)	−0.195 (2)	0.248 (2)	0.098
C(4)	0.167 (2)	−0.196 (3)	0.068 (2)	0.089
C(5)	0.044 (2)	0.045 (2)	0.116 (2)	0.075
C(6)	0.299 (3)	−0.047 (3)	0.094 (2)	0.105
C(7)	−0.056 (3)	0.072 (2)	0.361 (2)	0.075
C(8)	0.183 (3)	−0.002 (2)	0.383 (2)	0.087
C(9)	0.032 (3)	−0.152 (2)	0.416 (2)	0.085
C(10)	−0.1604 (18)	−0.0729 (19)	0.2452 (15)	0.055
C(111)	−0.3024 (18)	−0.2901 (19)	0.3403 (13)	0.056 (6)
C(112)	−0.367 (2)	−0.393 (2)	0.373 (1)	0.070 (7)
C(113)	−0.499 (3)	−0.337 (3)	0.433 (2)	0.098 (9)
C(114)	−0.493 (3)	−0.266 (3)	0.501 (2)	0.12 (1)
C(115)	−0.428 (3)	−0.167 (3)	0.474 (2)	0.098 (9)
C(116)	−0.295 (2)	−0.219 (2)	0.414 (1)	0.072 (7)
C(121)	−0.1855 (19)	−0.3569 (20)	0.1585 (14)	0.061 (6)
C(122)	−0.273 (2)	−0.434 (2)	0.154 (2)	0.074 (7)
C(123)	−0.291 (3)	−0.449 (3)	0.063 (2)	0.12 (1)
C(124)	−0.316 (3)	−0.341 (3)	0.029 (2)	0.15 (1)
C(125)	−0.220 (3)	−0.277 (3)	0.014 (2)	0.12 (1)
C(126)	−0.209 (3)	−0.252 (3)	0.108 (2)	0.16 (1)
C(131)	−0.0832 (18)	−0.4844 (18)	0.2834 (13)	0.052 (5)
C(132)	−0.0424 (18)	−0.4847 (19)	0.3669 (13)	0.055 (6)
C(133)	0.019 (2)	−0.608 (2)	0.389 (2)	0.091 (8)
C(134)	0.128 (3)	−0.668 (3)	0.321 (2)	0.108 (9)
C(135)	0.088 (2)	−0.675 (3)	0.237 (2)	0.096 (9)
C(136)	0.029 (2)	−0.547 (2)	0.211 (2)	0.076 (7)
C(141)	−0.375 (3)	0.102 (4)	0.251 (2)	0.13 (1)
C(142)	−0.379 (3)	0.081 (3)	0.151 (2)	0.15 (1)
C(143)	−0.532 (5)	0.177 (5)	0.176 (3)	0.22 (2)
C(144)	−0.488 (4)	0.273 (4)	0.161 (3)	0.18 (2)
C(145)	−0.467 (4)	0.303 (4)	0.241 (3)	0.20 (2)
C(146)	−0.330 (5)	0.186 (5)	0.241 (3)	0.21 (2)
H(1)	0.09933	−0.33079	0.24162	0.050
H(2)	0.14877	0.02402	0.23689	0.050

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

hedral, with the hydride ligands bridging Os–Os and Os–Pt edges, as expected from the ^1H NMR data. The hydride ligand sites were not observed crystallographically but were determined by using potential energy minimization procedures.[18] As is found in related unsaturated species[10,13] the hydride-bridged Os(2)–Os(3) separation of 2.752 (1) Å is anomalously short for an Os(μ-H)Os unit and may indicate localization of unsaturation along this edge. **3a** has an idealized mirror plane passing through Pt, Os(1), P, C(10), N, and the hydride ligands.

It is noteworthy that the isocyanide ligand in **3a** is bonded to the Pt atom, since for isomer A of complex **2a** the spectroscopic evidence clearly shows this ligand is bonded to an Os center. There is thus a transfer, from Os to Pt, of the RNC ligand in the decarbonylation of the butterfly adduct **2a** as it closes giving the tetrahedral unsaturated complex **3a**. At this stage we could not discount the possibility that one of the minor isomers, B or C, of **2a** had a Pt-bonded RNC group and that closure occurs via these isomers as intermediates. However since complex **3**, like **1**, is an unsaturated 58-electron species, high reactivity with two-electron donors was expected. Treatment of **3a** or **3b** with CO either at ambient temperature or at 195 K resulted in a rapid color change from dark green to yellow indicative of the formation of a butterfly adduct. Quite surprisingly the high-field signals in the ^1H NMR spectrum of this reaction mixture *were identical* with those of isomer A of **2a,b**. No resonances due to other species were observed, though on standing at ambient temperatures signals due to isomer B soon appear. There is thus a facile transfer of RNC back from Pt to Os as the tetrahedral structure reopens, resulting in sole formation of the most stable isomer of **2a,b**, i.e., isomer A. This result leads us to suggest that no isomers of **2a** or **2b** have Pt-bound RNC groups since such species would be the expected initial products from treatment of **3** with CO, and they are not observed.

Table III. Important Bond Lengths (Å) and Bond Angles (deg) for $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CyNC)$ (3a)

Bond Lengths

Os(1)–Os(2)	2.745 (1) [2.777 (1)][a]	Os(1)–C(3)	1.87 (3)
Os(1)–Os(3)	2.742 (1) [2.741 (1)]	Os(2)–C(4)	1.89 (3)
Os(2)–Os(3)	2.752 (1) [2.789 (1)]	Os(2)–C(5)	1.89 (3)
Pt–Os(1)	2.844 (1) [2.863 (1)]	Os(2)–C(6)	1.85 (3)
Pt–Os(2)	2.773 (1) [2.791 (1)]	Os(3)–C(7)	1.87 (3)
Pt–Os(3)	2.781 (1) [2.832 (1)]	Os(3)–C(8)	1.86 (3)
Pt–P	2.346 (6)	Os(3)–C(9)	1.84 (3)
Pt–C(10)	1.85 (3)	P–C(111)	1.84 (3)
Os(1)–C(1)	1.83 (3)	P–C(121)	1.82 (3)
Os(1)–C(2)	1.84 (3)	P–C(131)	1.80 (3)
C(10)–N	1.14 (4)		

C–O(carbonyl) = 1.16 [1] (mean)

Bond Angles

Os(1)–Pt–Os(2)	58.5 (1)	Pt–Os(2)–Os(1)	62.1 (1)
Os(1)–Pt–Os(3)	58.3 (1)	Pt–Os(2)–Os(3)	60.4 (1)
Os(2)–Pt–Os(3)	59.4 (1)	Os(1)–Os(2)–Os(3)	59.8 (1)
Pt–Os(1)–Os(2)	59.4 (1)	Pt–Os(3)–Os(1)	62.0 (1)
Pt–Os(1)–Os(3)	59.7 (1)	Pt–Os(3)–Os(2)	60.1 (1)
Os(2)–Os(1)–Os(3)	60.2 (1)	Os(1)–Os(3)–Os(2)	59.9 (1)
C(10)–Pt–P	93.5 (7)	P–Pt–H(1)	82.2 (2)
Pt–C(10)–N	175 (2)	C(10)–N–C(141)	166 (3)

Os–C–O = 176 [1] (mean)

[a] Values in square parentheses are those corresponding distances in complex 1.[10]

Rapid exchange of CO ligands between Pt and Os centers, in a very rapid low-energy six-site fluxional process, has been observed for complex **2c**.[13] This complex has a structure similar to that suggested for isomer B, and such a process operating in **2a,b** could account for the facile Os/Pt isocyanide transfer. While there is little evidence for such an exchange process in isomer A of **2a**, it is important to note that were the isocyanide one of those ligands involved in the "merry-go-round", such a six-site exchange would not be a degenerate process and the various intermediates would not necessarily be equienergetic and hence equally populated. We have suggested that the six-site exchange in **2c** occurs via a closo or "semi-closo" transition state,[13] and it is interesting to speculate that ejection of a CO ligand from such a transition state of **2a,b** could provide a reaction pathway leading to closure of the 60-electron butterfly adduct and formation of the tetrahedral complexes **3**.

The facile loss of CO from complexes **2a,b** to regenerate the ligand-substituted unsaturated precursor parallels the

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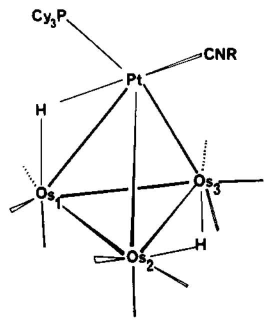
behavior of other unsaturated clusters. For example, the phosphine adducts of $Os_3(\mu\text{-}H)_2(CO)_{10}$ readily lose CO on thermolysis, giving the unsaturated PR_3-substituted species $Os_3(\mu\text{-}H)_2(CO)_9(PR_3)$ (R_3 = Ph_3, Me_2Ph),[19] which have the PR_3 group in an equatorial position.[20] Adams and Golembeski[7,8] have demonstrated analogous reactivity with isocyanide ligands. Vahrenkamp has also shown[21] that the unsaturated square-planar clusters $Fe_4(CO)_{11}(\mu_4\text{-}PR)_2$ can undergo stepwise ligand addition/elimination reactions via saturated and unsaturated intermediates, resulting in multisubstitution by PR_3 or RNC groups. There thus appears to be some inherent stability arising in these systems which favors the unsaturated configuration.

The reactivity of the unsaturated clusters **1** and **3** with "soft" nucleophiles is likely to be dominated by frontier orbital effects. The HOMO and LUMO of these species are localized on the hydride-bridged Os–Os vector,[22] and thus these metal centers are expected to be the initial sites of nucleophilic attack. This appears reasonable from the products isolated from reaction of **1** with CO and PR_3,[11,12] where the incoming ligand is coordinated to an Os center. If we assume similar site selectivity in the reaction of **3a** with CO, the product we observe must then arise from a rapid molecular rearrangement of the initially formed species. Caution should therefore be exercised in interpreting reaction pathways from the observed products in these systems.



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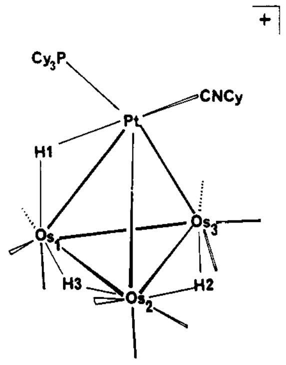

4

In situ treatment of **3a** with CF_3COOH or $HBF_4 \cdot Et_2O$ gives rise to the cationic trihydrido species **4** which has been identified spectroscopically. The BF_4^- salt shows three high-field ^1H resonances at −13.13, −13.29 (J(Pt–H) = 547; J(P–H) = 7.2 Hz), and −13.47 ppm (J(Pt–H) = 21 Hz). Protonation occurs along an Os–Os edge as previously observed for complex **1**,[13] and the fluxional behavior of **4** is very similar to that observed in $[Os_3Pt(\mu\text{-}H)_3(CO)_{10}(PCy_3)]^+$,[13] in that the two Os(μ-H)Os protons at −13.13 and −13.47 ppm broaden on warming, indicating exchange, and coalesce at ca. 330 K, while the Os(μ-H)Pt resonance at −13.29 ppm remains sharp throughout. The resonance at −13.47 ppm can be attributed to the proton H3 from its significant ^{195}Pt coupling.[13]

Table IV. Final Positional Parameters (Fractional Coordinates) with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters (U_{eq}, Å^2) for $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CNCy)$ (5)[a]

	x/a	y/b	z/c	U_{eq}
Os(1)	−0.06208 (6)	0.04138 (8)	−0.17232 (5)	0.035
Os(2)	−0.01240 (6)	0.08127 (8)	−0.33401 (4)	0.032
Os(3)	0.08391 (7)	0.26800 (8)	−0.17490 (5)	0.040
Pt	0.17484 (6)	0.09869 (7)	−0.22009 (4)	0.025
N	0.3887 (15)	0.2658 (17)	−0.2809 (12)	0.056
P	0.2784 (4)	−0.0036 (4)	−0.1930 (3)	0.026
C(1)	−0.0018 (18)	0.0945 (20)	−0.0541 (13)	0.048
C(2)	−0.1539 (18)	−0.1238 (23)	−0.1927 (15)	0.057
C(3)	−0.1883 (19)	0.0922 (29)	−0.1443 (13)	0.088
C(4)	−0.1440 (17)	0.0325 (20)	−0.4159 (11)	0.045
C(5)	0.1001 (17)	0.1685 (20)	−0.3885 (12)	0.042
C(6)	0.0266 (15)	−0.0435 (19)	−0.3757 (12)	0.040
C(7)	0.003 (2)	0.357 (2)	−0.111 (2)	0.059 (6)
C(8)	0.190 (2)	0.392 (2)	−0.209 (2)	0.062
C(9)	0.206 (2)	0.308 (2)	−0.083 (1)	0.066
C(10)	0.3099 (17)	0.2065 (19)	−0.2581 (12)	0.041
C(11)	−0.0606 (17)	0.2184 (19)	−0.2779 (15)	0.060
C(111)	0.1761 (14)	−0.1470 (17)	−0.1837 (11)	0.029
C(112)	0.0920 (18)	−0.2294 (20)	−0.2582 (14)	0.054
C(113)	−0.011 (2)	−0.340 (2)	−0.241 (2)	0.076
C(114)	0.051 (2)	−0.397 (2)	−0.203 (2)	0.071
C(115)	0.1385 (18)	−0.3113 (21)	−0.1288 (15)	0.059
C(116)	0.2368 (17)	−0.2078 (19)	−0.1441 (13)	0.050
C(121)	0.3776 (14)	−0.0260 (16)	−0.2713 (9)	0.026
C(122)	0.3167 (17)	−0.0806 (20)	−0.3618 (10)	0.044
C(123)	0.4094 (19)	−0.0764 (22)	−0.4226 (12)	0.055
C(124)	0.4867 (19)	−0.1277 (23)	−0.4087 (13)	0.059
C(125)	0.5446 (19)	−0.0822 (26)	−0.3188 (14)	0.075
C(126)	0.4505 (17)	−0.0944 (20)	−0.2597 (13)	0.049
C(131)	0.3858 (14)	0.0794 (18)	−0.0920 (10)	0.034
C(132)	0.4820 (17)	0.2050 (18)	−0.0893 (12)	0.040
C(133)	0.5747 (18)	0.2678 (21)	−0.0085 (14)	0.055
C(134)	0.509 (2)	0.276 (3)	0.071 (1)	0.072
C(135)	0.4151 (19)	0.1516 (27)	0.0683 (14)	0.070
C(136)	0.3204 (16)	0.0969 (21)	−0.0141 (11)	0.047
C(141)	0.477 (2)	0.350 (2)	−0.311 (2)	0.061
C(142)	0.553 (3)	0.461 (2)	−0.237 (2)	0.101
C(143)	0.637 (4)	0.445 (5)	−0.185 (3)	0.145
C(144)	0.715 (3)	0.410 (5)	−0.226 (4)	0.156
C(145)	0.646 (4)	0.297 (4)	−0.283 (4)	0.184
C(146)	0.558 (3)	0.306 (3)	−0.349 (2)	0.109
O(1)	0.0347 (18)	0.1273 (21)	0.0140 (10)	0.104
O(2)	−0.2144 (15)	−0.2179 (17)	−0.1985 (13)	0.083
O(3)	−0.2604 (14)	0.1241 (19)	−0.1305 (10)	0.091
O(4)	−0.2246 (13)	0.0055 (19)	−0.4671 (10)	0.087
O(5)	0.1693 (14)	0.2261 (17)	−0.4190 (10)	0.076
O(6)	0.0226 (13)	−0.1388 (15)	−0.4167 (10)	0.060
O(7)	−0.0546 (17)	0.3981 (18)	−0.0770 (12)	0.102
O(8)	0.2521 (15)	0.4642 (16)	−0.2333 (13)	0.085
O(9)	0.2789 (18)	0.3443 (19)	−0.0241 (12)	0.109
H(1)	−0.13090	−0.0061	−0.28363	0.050
H(2)	0.06119	−0.00782	−0.17957	0.050

[a] $U_{eq} = {}^1/_3 \sum_i \sum_j U_{jj} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

The reactivity of **3a** with CH_2N_2 was investigated with the goal of synthesizing species arising from isocyanide insertion into the μ-CH_2 unit. Several examples of C–C bond formation by CO insertion into cluster-bound methylene groups have been recently reported.[23–26] Treatment of **3a** with excess CH_2N_2 afforded high yields of the orange-red methylene complex $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CyNC)$ (**5**). Only one isomer of this complex was observed, in contrast to the analogous reaction of CH_2N_2 with **1** where two isomers of $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}(PCy_3)$ are observed. These two isomers differ in the hydride ligand disposition in that the yellow isomer has two Os(μ-H)Os protons, while the more stable red isomer has one Os(μ-H)Os and one Os(μ-H)Pt proton.[11]

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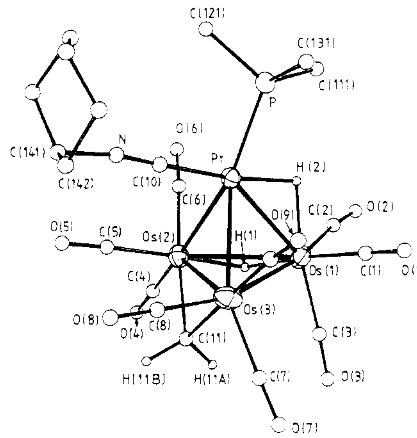
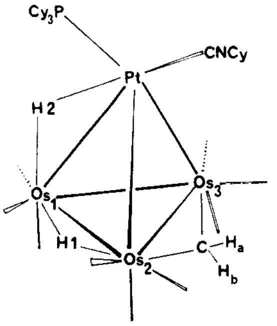


Figure 5. Molecular geometry and atomic labeling scheme for $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CyNC)$ (**5**). Phosphine cyclohexyl groups omitted for clarity.

Complex **5** is related to the red isomer, showing signals at −15.87 (J(Pt–H) = 534, J(P–H) = 7.3 Hz) and −21.82 ppm (J(Pt–H) = 22 Hz) in the ^1H NMR spectrum, indicative of Os(μ-H)Pt and Os(μ-H)Os protons respectively. The two inequivalent methylene protons H_a and H_b resonate at 6.61 and 7.02 ppm.

The molecular structure of **5**, determined from a single crystal X-ray study is illustrated in Figure 5, with a stereoview given in Figure 6 (supplementary material). Atomic coordinates and important metrical parameters are supplied in Tables IV and V, respectively. The structure is closely similar to the red methylene adduct of **1**.[11] The tetrahedral Os_3Pt core is maintained, and the general increase in metal–metal separations is consistent with the relief of unsaturation. A nearly linear (C(10)–N–C(141) = 171 (2)°) terminal CyNC group remains ligated to the Pt center, while a slightly asymmetric methylene group bridges the Os(2)–Os(3) bond (2.841 (2) Å), viz., Os(2)–C(11) = 2.08 (3) and Os(3)–C(11) = 2.20 (3) Å. These two ligands thus lie about the same face of the tetrahedron, i.e., Pt–Os(2)–Os(3). The carbonyl carbon atoms C(6) and C(9) trans to C(11) are approximately coplanar with this metal face. There is a weak semibridging interaction between these carbonyls and the Pt atom as can be seen in the relatively short Pt···C(6) = 2.78 (2) and Pt···C(9) = 2.87 (2) Å contact distances, and the slightly bent disposition of these groups, viz., Os(2)–C(6)–O(6) = 162 (2) and Os(3)–C(9)–O(9) = 172 (2)°. The methylene hydrogen positions were not observed crystallographically but are calculated assuming pseudotetrahedral geometry for C(11). The hydridic protons were likewise included at calculated positions by using the program HYDEX,[18] these positions agreeing with the spectroscopic data in that one hydride bridges an Os–Os edge and the other an Os–Pt edge.



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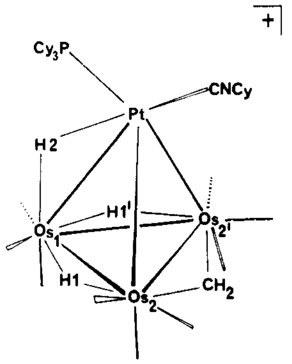

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Table V. Important Bond Lengths (Å) and Bond Angles (deg) for $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CyNC)$ (5)

	Bond Lengths		
Os(1)–Os(2)	2.965 (2)	Os(2)–C(4)	1.86 (2)
Os(1)–Os(3)	2.796 (2)	Os(2)–C(5)	1.86 (3)
Os(2)–Os(3)	2.841 (2)	Os(2)–C(6)	1.83 (3)
Pt–Os(1)	2.865 (1)	Os(3)–C(7)	1.92 (3)
Pt–Os(2)	2.858 (1)	Os(3)–C(8)	1.89 (3)
Pt–Os(3)	2.787 (2)	Os(3)–C(9)	1.92 (3)
Os(1)–C(1)	1.92 (2)	Os(2)–C(11)	2.08 (3)
Os(1)–C(2)	1.91 (3)	Os(3)–C(11)	2.20 (3)
Os(1)–C(3)	1.92 (3)	Pt–C(10)	1.95 (3)
Pt–P	2.322 (5)	C(10)–N	1.12 (3)
Pt···C(6)	2.78 (2)	Pt···C(9)	2.87 (2)
	C–O(carbonyl) = 1.14 [1] (mean)		
	Bond Angles		
Os(1)–Pt–Os(2)	62.4 (1)	Pt–Os(2)–Os(1)	58.9 (1)
Os(1)–Pt–Os(3)	59.3 (1)	Pt–Os(2)–Os(3)	58.6 (1)
Os(2)–Pt–Os(3)	60.4 (1)	Os(1)–Os(2)–Os(3)	57.5 (1)
Pt–Os(1)–Os(2)	58.7 (1)	Pt–Os(3)–Os(1)	61.8 (1)
Pt–Os(1)–Os(3)	59.0 (1)	Pt–Os(3)–Os(2)	61.0 (1)
Os(2)–Os(1)–Os(3)	59.0 (1)	Os(1)–Os(3)–Os(2)	63.5 (1)
C(10)–Pt–P	95.5 (6)	P–Pt–H(2)	77.7 (2)
Os(2)–C(11)–Os(3)	83.2 (8)	C(10)–N–C(141)	171 (2)
Os(2)–C(6)–O(6)	162 (2)	Os(3)–C(9)–O(9)	172 (2)
Pt–C(10)–N	178 (2)		
	Remaining Os–C–O = 176 [1] (mean)		

The coordination geometry of the Os atoms in complexes **3a** and **5** is essentially octahedral (ignoring the bridged metal–metal vectors), while that of the Pt atoms approximates to trigonal bipyramidal. Like the starting precursor, these two complexes are unusual in that the Pt atom is behaving as an 18-electron metal, resulting in the expected cluster valence electron counts,[27] i.e. 58 for **3a** (and **1**) as an unsaturated tetrahedron and 60 for **5** as a saturated tetrahedron. Normally platinum adopts a pseudo-square-planar geometry in cluster compounds of this type and behaves as a 16-electron center, as, for example, in complexes **2c**,[11] **2d**,[12] or $Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2$.[28]

All attempts to induce intramolecular isocyanide insertion into the methylene group of complex **5** failed. Thermolysis produced no tractable products, and **5** was unreactive to CO (50 atm) at ambient temperature. More forcing conditions resulting in cluster fragmentation, and likewise on reaction with PPh_3 at 90 °C numerous products were formed, as determined by TLC. These reactions were not investigated further. Protonation of **5** with CF_3COOH gave the cation $[Os_3Pt(\mu\text{-}H)_3(\mu\text{-}CH_2)(CO)_9(PCy_3)(CyNC)]^+$ (**6**) as determined from the ^1H NMR spectrum of the reaction mixture. High-field signals were observed at −17.73 (J(Pt–H) = 490 Hz) and −21.67 ppm (J(Pt–H) = 11 Hz) in the ratio 1:2, indicative of a structure with one Os(μ-H)Pt and two equivalent Os(μ-H)Os protons, respectively.

Finally we note that Geoffroy and co-workers[29] have recently reported a structure of a methylene-bridged cluster $Os_3Pt(\mu\text{-}CH_2)(CO)_{11}(PPh_3)_2$ with a "spiked-triangular" metal geometry and with the methylene ligand bridging an Os–Pt bond. This complex has 62 valence electrons and an approximately square-planar Pt atom and is probably best described as an equatorially substituted product of $Os_3(CO)_{12}$ with the inorganic "ethylene" $H_2C{=}Pt(PPh_3)_2$.

Experimental Section

General experimental techniques and instrumentation were as previously reported.[30] $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ was prepared

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Table VI. Experimental Data for Crystallographic Study

	3a	**5**
compd formula	$C_{34}H_{46}NO_9Os_3PPt$	$C_{35}H_{48}NO_9Os_3PPt$
M_r	1409.4	1423.4
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$
cryst system	triclinic	triclinic
a/Å	11.283 (3)	12.189 (3)
b/Å	11.697 (5)	13.180 (4)
c/Å	16.367 (8)	16.901 (6)
α/deg	89.23 (4)	108.31 (4)
β/deg	74.79 (3)	90.62 (4)
γ/deg	76.94 (3)	114.20 (2)
V/Å^3	2028 (1)	2320 (1)
Z	2	2
D_{calcd}/g cm^{-3}	2.31	2.04
F(000)	1300	1316
μ(Mo Kα)/cm^{-1}	129.4	113.1
T/K	298	
scan mode	$\theta/2\theta$	
θ range/deg	$2 < \theta < 24$	$2 < \theta < 27.5$
cryst size/mm	0.35 × 0.3 × 0.2	0.25 × 0.3 × 0.4
range of trans coeff corr	0.71/1.77	0.59/1.82
no. of data collected	6710	11119
no. of unique data	6345	10619
std reflctns	703, $\bar{5}\bar{1}\bar{9}$	603, $\bar{3}19$, $3\bar{6}11$
observability criterion n ($I > n\sigma(I)$)	2.5	2.5
no. of data in refinement	4055	6659
no. of refined parameters	151/250	262/284
final R	0.055	0.059
R_w	0.053	0.080
largest remaining feature in electron density map, e Å^{-3}	+1.64 (max), −2.38 (min)	+3.36 (max), −4.08 (min)
shift/esd in last cycle	0.41 (max), 0.07 (av)	0.06 (max), 0.01 (av)

as described previously.[10] CyNC and t-BuNC were used as received from Aldrich Chemicals. NMR studies on the isocyanide adducts **2a** and **2b** were carried out in situ by addition of solutions of known concentration of the isocyanide in $CDCl_3$.

Preparation of $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CyNC)$ (3a). A solution of **1** (0.153 g, 0.12 mmol) in hexanes (50 mL) was treated with CyNC (0.58 mL of a 0.2 M solution in hexanes). The dark green color of **1** was discharged giving a yellow solution, which was refluxed under a dinitrogen purge for 1.5 h. Concentration of the dark green solution afforded crystals of $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CyNC)$ (**3a**) (0.139 g, 84% yield): IR (cyclohexane) ν_{max}(CN) 2177 (br), ν_{max}(CO) 2064 (m), 2035 (s), 2012 (s), 1983 (s), 1959 (m), 1952 (m), 1935 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 233 K) δ 3.75–1.23 (m, 44 H, C_6H_{11}), −8.01 (s, Os(μ-H)Os), −11.35 (d, 1 H, Os(μ-H)Pt, J(Pt–H) = 544, J(P–H) = 9.1 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 233 K) 192.8 (s, 2 C, OsCO), 185.3 (s, 2 C, OsCO), 182.2 (s, 2 C, OsCO), 180.4 (s, 1 C, OsCO), 179.7 (s, 2 C, OsCO), 115.3 (s, br, 1 C, CyNC), 55.7 and 36.1–24.0 ppm (m, C_6H_{11}). Anal. Calcd for $C_{34}H_{46}NO_9Os_3PPt$: C, 28.98; H, 3.29; N, 0.99. Found: C, 29.09; H, 3.11; N, 0.92.

In a similar fashion treatment of **1** (0.154 g, 0.116 mmol) with t-BuNC afforded **3b** (0.143 g, 87% yield): IR (cyclohexane) ν_{max}(CN) 2169 (br), ν_{max}(CO) 2064 (m), 2035 (s), 2012 (s), 1983 (s), 1958 (m), 1952 (m), 1935 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 233 K) δ 1.78–1.24 (m, 42 H, C_6H_{11} and CH_3), −7.99 (s, 1 H, Os(μ-H)Os, J(Pt–H) = 5.7 Hz), −11.47 (d, 1 H, Os(μ-H)Pt, J(Pt–H) = 539, J(P–H) = 9.4 Hz). Anal. Calcd for $C_{32}H_{44}NO_9Os_3PPt$: C, 27.78; H, 3.2; N, 1.01; P, 2.24. Found: C, 27.73; H, 3.10; N, 0.93; P, 2.76.

^1H NMR Data for $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)(RNC)$ ($CDCl_3$, 223 K). For NMR data on isomer A of **2a** see Table I. **2a** (**R = Cy**): isomer B, δ −11.59 (d, 1 H, Os(μ-H)Pt, J(Pt–H) = 503, J(P–H) = 11 Hz), −17.56 (d, 1 H, Os(μ-H)Os, J(Pt–H) = 26, J(P–H) = 1.5 Hz); isomer C, δ −9.70 (d, Os(μ-H)Pt, J(Pt–H) = 570, J(P–H) = 15 Hz), −18.94 (s, Os(μ-H)Os, J(Pt–H) = 16 Hz). **2b** (**R = t-Bu**); isomer A, δ −9.74 (d, 1 H, Os(μ-H)Pt, J(Pt–H) = 567, J(P–H) = 14.6 Hz), −17.57 (s, 1 H, Os(μ-H)Os); isomer B, −11.60 (d, 1 H, Os(μ-H)Pt, J(Pt–H) = 503, J(P–H) = 10.8 Hz); isomer C, −9.65 (d, 1 H, Os(μ-H)Pt, J(P–H) = 12.0 Hz), −18.98 (s, 1 H, Os(μ-H)Os).

Preparation of $[Os_3Pt(\mu\text{-}H)_3(CO)_9(PCy_3)(CyNC)]^+BF_4^-$ (4). A solution of **3a** (0.06 g, 0.043 mmol) in CH_2Cl_2 (1.5 mL) was treated with excess $HBF_4 \cdot Et_2O$ at room temperature. The solution changed color from dark green to dark purple and the product identified spectroscopically: IR (CH_2Cl_2) δ_{max}(CN) 2202 (br), ν_{max}(CO) 2111 (m), 2088 (vs), 2062 (vs), 2036 (s), 2019 (s), 1990 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 298 K) δ 3.81–1.36 (m, 44 H, C_6H_{11}), −13.13 (s, 1 H, Os(μ-H)Os), −13.29 (d, 1 H, Os(μ-H)Pt, J(Pt–H) = 547, J(P–H) = 7.2 Hz), −13.47 (s, 1 H, Os(μ-H)Os, J(Pt–H) = 21 Hz); ^{31}P NMR ($CDCl_3$, 298 K) 65.6 ppm (J(Pt–P) = 2456 Hz).

Preparation of $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CyNC)$ (5). A solution of **3a** (0.150 g, 0.107 mmol) in toluene (15 mL) was treated dropwise with a solution of diazomethane in diethyl ether (prepared from an Aldrich Diazald kit) at 273 K until the dark green color of the starting material gave way to an orange solution. Evaporation of this solution in vacuo and recrystallization of the residue from diethyl ether afforded red crystals of the product **5** (0.127 g, 83%): IR (cyclohexane) ν_{max}(CN) 2181 (br), ν_{max}(CO) 2068 (m), 2047 (s), 2016 (s), 1989 (s), 1973 (s), 1954 (m), 1950 (m), 1925 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 298 K) δ 7.02 (m, 1 H, CH_2), 6.61 (d of d, 1 H, CH_2, J(H–H) = 6.0, 2.3 Hz), 3.96–1.12 (m, 44 H, C_6H_{11}), −15.87 (d, 1 H, Os(μ-H)Pt, J(Pt–H) = 534, J(P–H) = 7.3 Hz), −21.82 (s, 1 H, Os(μ-H)Os, J(Pt–H) = 22 Hz). Anal. Calcd for $C_{35}H_{48}NO_9Os_3PPt$: C, 29.54; H, 3.37; N, 0.98. Found: C, 29.79; H, 3.22; N, 0.79.

Crystal Structure Determination. Details of data collection procedures and structure refinement are given in Table VI. Crystals of **3a** were grown as black prisms from hexane and crystals of **5** as red-orange blocks from diethyl ether. Data were collected at ambient temperature on an Enraf-Nonius CAD4F automated diffractometer, with graphite-monochromated X-radiation (λ = 0.71069 Å). Unit cell parameters were determined by refinement of the setting angles ($\theta > 12°$) of 25 reflections. Standards were measured every 2 h during data collection; no significant decay was observed for **3a**, and a linear correction corresponding to a 5% decay over 10000 reflections was applied to the data set for **5**. Lorentz/polarization and absorption (DIFABS[31]) corrections were applied to both data sets. No systematic absences were observed, and E statistics indicated the centrosymmetric space group $P\bar{1}$ for both compounds. The structures were solved by direct methods (MITHRIL[32]) and subsequent electron density difference syntheses. All non-hydrogen atoms in complex **5** were allowed anisotropic thermal motion, except for C(7) whose anisotropic parameter became nonpositive definite during refinement procedures. For complex **3a** all non-hydrogen atoms except those carbon atoms of the cyclohexyl groups were allowed anisotropic motion. Some disorder in the cyclohexyl ring, C(141)–C(146), of **3a** was evident in unrealistic C–C bond lengths, but no disordered model could be satisfactorily refined and only the major components were included in the final analysis. For complex **5** there was evidence of a disordered molecule of diethyl ether of solvation, but again no satisfactory refinement was feasible and this molecule was not included in the analysis. This resulted in rather high residuals. Cyclohexyl hydrogen atoms were included at calculated positions (C–H = 1.073 Å), as were the hydridic hydrogens (HYDEX;[18] Os–H, Pt–H = ca. 1.85 Å), and both were held fixed during refinement with fixed isotropic (0.05 Å^2) thermal parameters. Refinement was by full-matrix least squares. Due to matrix size limitations the parameter list was divided into two sections and each refined separately. The function minimized was $w(|F_o| - |F_c|)^2$ with the weighting function $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. Neutral atom scattering factors were taken from ref 33 with corrections applied for anomalous dispersion. All calculations were carried out on a Gould-SEL 32/27 mini computer using the GX suite of programs.[34]

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Registry No. **1**, 68091-56-5; **2a** (isomer A), 112653-30-2; **2a** (isomer B), 112548-98-8; **2a** (isomer C), 112548-97-7; **2b** (isomer

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A), 112548-95-5; **2b** (isomer B), 112548-96-6; **2b** (isomer C), 112652-65-0; **3a**, 112548-92-2; **3b**, 112548-93-3; **4**, 112548-94-4; **5**, 112574-99-9; Os, 7440-04-2; Pt, 7440-06-4.

Supplementary Material Available: Stereoviews (Figures 4 and 6) of **3a** and **5** and tables of anisotropic thermal parameters and calculated hydrogen atom positional parameters and complete listings of bond length and angles (13 pages); listings of calculated and observed structure factors (52 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Reactivity of Molybdenum–Dienyl Complexes

Te-Wei Lee and Rai-Shung Liu*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

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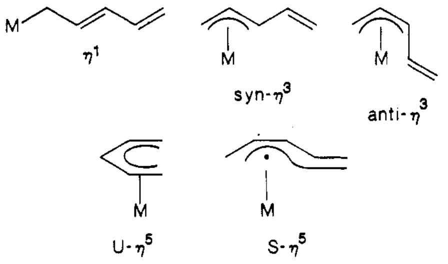
The reaction between $CpMo(CO)_3Na$ and 1-chloropenta-2,4-diene or 1-chlorohexa-2,4-diene yields $CpMo(CO)_3(\eta^1$-2,4-pentadien-1-yl) (**1**) or $CpMo(CO)_3(\eta^1$-2,4-hexadien-1-yl) (**2**), respectively. These η^1 complexes readily undergo an $\eta^1 \rightarrow$ syn-$\eta^3 \rightarrow \eta^5$ transformation by chemical or photolytic activation, and the resulting products are characterized by appropriate physical methods. Photolysis of $CpMo(CO)_2$(*syn*-η^3-2,4-hexadien-1-yl) (**10**) gives rise to $CpMo(CO)_2$(*syn*-η^3-1-methyl-2,4-pentadien-1-yl) (**11**) in addition to the two isomeric η^5 forms $CpMo(CO)(\eta^5$-2,4-hexadien-1-yl) (**15**) and $CpMo(CO)(\eta^5$-1-methyl-2,4-pentadien-1-yl) (**16**). Preparation and characterization of the corresponding phosphine derivatives in η^1 and syn-η^3 configurations are described. At ambient temperatures, **1** readily undergoes [4 + 2] cycloaddition with dienophiles such as tetracyanoethylene and maleic anhydride.

Introduction

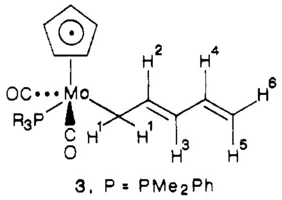
Transition-metal–allyl complexes have been the subject of intensive studies for many years because of their remarkable activity in reaction chemistry. Notable examples are η^1- and η^3-allyls of iron[1] and molybdenum[2] complexes that have proven to be very useful reagents in synthetic chemistry. In recent years, there has been a growing interest in the preparation of transition-metal–pentadienyl complexes.[3] In comparison with their allyl analogues, the chemistry of metal–pentadienyl complexes should in principle be more intriguing because of the various geometries possible for the pentadienyl ligand bound to the metal center as depicted in Chart I. One may reasonably anticipate a wide range of chemical versatility for these complexes. In this paper,[4] we describe the synthesis of a family of molybdenum–pentadienyl complexes in the η^1, syn-η^3, and S-η^5 configurations as well as their phosphine derivatives. The reaction chemistry of $CpMo(CO)_3(\eta^1$-pentadienyl) (**1**) with the dienophiles tetracyanoethylene and maleic anhydride is also described.

Chart I



Results and Discussion

The reaction between $CpMo(CO)_3Na$ and *trans*-1-chloropenta-2,4-diene at −78 °C for 6 h gave a yellow crystalline solid of $CpMo(CO)_3(\eta^1$-pentadienyl) (**1**) in good yield after workup. Preparation of the 2,4-hexadien-1-yl analogue $CpMo(CO)_3(\eta^1$-2,4-hexadien-1-yl) (**2**) is easily achieved through stirring of a tetrahydrofuran solution of $CpMo(CO)_3Na$ and *trans*-1-chloro-2,4-hexadiene; the yield is 57%. These η^1 complexes readily undergo ligand substitution with the phosphines PMe_2Ph and PEt_3. Stirring of **1** with PMe_2Ph or PEt_3 at 23 °C gave high yields of $CpMo(CO)_2(PMe_2Ph)(\eta^1$-pentadienyl) (**3**) or $CpMo(CO)_2(PEt_3)(\eta^1$-pentadienyl) (**4**), respectively. Purification of these compounds by column chromatography gave analytically pure yellow oils. Attempts to obtain the trimethylphosphine analogues were not successful in similar reactions. For **3** and **4**, the ^{13}C NMR spectra reveal that the phosphine ligand is trans to the pentadienyl group. The resonances of the two CO ligands are equivalent and show a single doublet with $J_{PC} \simeq$ 22 Hz. The facile CO



3, P = PMe_2Ph
4, P = PEt_3

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