Synthesis, Structures, Isomerism, and Dynamic Behavior of Metalated Derivatives of Methyl-Substituted Pyrroles in Triruthenium Clusters

Alejandro J. Arce,* Rubén Machado, Ysaura De Sanctis,
Mario V. Capparelli, and Reinaldo Atencio

*Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC),
Apartado 21827, Caracas 1020-A, Venezuela*

Jorge Manzur

*Departamento de Química, Universidad de Chile, Avenida Tupper 2069,
Casilla 2777, Santiago, Chile*

Antony J. Deeming

*Department of Chemistry, University College London, 20 Gordon Street,
London WC1H 0AJ, Great Britain*

Received October 3, 1996[⊗]

Direct thermal reaction of [$Ru_3(CO)_{12}$] with 1-methylpyrrole leads to the cluster [$Ru_3(\mu$-H)(μ_3,η^3-C_4H_3NMe)($CO)_9$] (**1**), in which metalation has occurred at the 3-position of the ring. In solution, two isomers, **1a**,**b**, detected by ^{1}H NMR at low temperature, are in dynamic equilibrium ([**1a**]/[**1b**] = 1.8 at 260 K in $CDCl_3$), and coalesced signals are observed above room temperature. Crystals of **1** deposited from the mixed isomer solution were shown by single-crystal X-ray structure determination to be those of isomer **1a**. The ligand μ_3,η^3-C_4H_3NMe in cluster **1a** is coordinated in a previously unidentified way to the Ru_3 triangle through σ-Ru−C bonds to two metal atoms and through an η^2-interaction to the third. A zwitterionic description with positive charge largely located at the NMe group and a negative charge delocalized on the metal atoms is presented. The dynamic equilibrium between **1a** and **1b** involves a hydride shift between Ru−Ru edges and a 1,2-double bond shift within the μ_3-ligand. Clusters [$Ru_3(\mu$-H){μ_3,η^3-$C_4H(Me)_2NMe$}($CO)_9$] (**2**) and [$Ru_3(\mu$-H){μ_3,η^3-$C_4H(Me)_2NH$}($CO)_9$] (**3**) obtained from 1,2,5-trimethylpyrrole and 2,5-dimethylpyrrole in refluxing THF adopt crystal structures corresponding to that of **1a** but, unlike **1**, exist in only one isomeric form in solution at low temperatures. However, different products are obtained from [$Ru_3(CO)_{12}$] and 2,5-dimethylpyrrole in refluxing toluene: [$Ru_3(\mu$-H){μ_3,η^3-CH=$C_4H_2(Me)N$}($CO)_9$] (**4**, X-ray structure reported) and [$Ru_3(\mu$-H){μ_3,η^2-$CHC_4H_2(Me)N$}-(μ-CO)($CO)_9$] (**5**), our proposed structure of which is based on spectroscopic evidence. Changing the solvent for the reaction has resulted in cleavage on the N−H bond to give N-bonded ligands, in activation of a methyl group, and in loss of H_2. Thermal treatment of **1a**,**b** in refluxing cyclohexane leads to a third isomer, [$Ru_3(\mu$-H$)_2(\mu_3,\eta^2$-C_4H_2NMe)($CO)_9$] (**6**), completely analogous to a known, structurally characterized Os complex. In more polar solvents, **6** reverts to a mixture of **1a** and **1b**.

Introduction

The reaction of 1-methylpyrrole with [$Os_3(CO)_{10}$-($MeCN)_2$] leads by metalation at the 2-position to the zwitterionic product [$Os_3(\mu$-H)(μ,η^1-C_4H_3NMe)($CO)_{10}$], in which the *N*-methylpyrrolyl ligand bridges through the 2-carbon as an alkylidene bridge (Scheme 1).[1a] This compound contrasts with the stoichiometrically equivalent furyl and thienyl complexes, which have μ,η^1,η^2-bridges of the vinyl type. We have shown that this 1-methylpyrrolyl isomer converts in solution very slowly at room temperature to an equilibrium mixture including isomers metalated at the 3-position.[1b] Decarbonylation of these 1-methylpyrrolyl complexes leads to the 1-methylpyrrol-2,3-yne complex [$Os_3(\mu$-H$)_2(\mu_3,\eta^2$-C_4H_2-NMe)($CO)_9$], the crystal structure of which shows that it contains a parallel pyrrolyne ligand.[2]

Seeking to explore the chemistry of pyrroles with the iron triad, we have now examined the chemistry of [Ru_3-($CO)_{12}$] with 1-methylpyrrole and the related heterocycles 1,2,5-trimethylpyrrole and 2,5-dimethylpyrrole. It is known that the chemistry of thiophenes with triosmium clusters leads exclusively to C−H activation (no ring opening),[1,3] whereas with triruthenium clusters both C−H and C−S cleavages take place.[4] With iron carbonyls, C−S cleavage dominates their chemistry with thiophenes.[5] In the light of these changes of chemistry between iron, ruthenium, and osmium, we anticipated

---

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

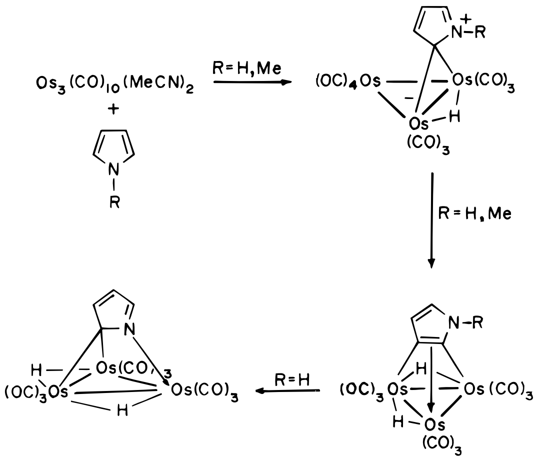
[1] (a) Arce, A. J.; Manzur, J.; Márquez, M.; De Sanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1991**, *412*, 177. (b) Arce, A. J.; Manzur, J.; Márquez, M.; De Sanctis, Y., unpublished results.

[2] Deeming, A. J.; Arce, A. J.; De Sanctis, Y.; Day, M. W.; Hardcastle, K. I. *Organometallics* **1989**, *8*, 1408.

[3] Arce, A. J.; Deeming, A. J.; De Sanctis, Y.; Machado, R.; Manzur, J.; Rivas, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1568.

S0276-7333(96)00847-3 CCC: $14.00

Scheme 1

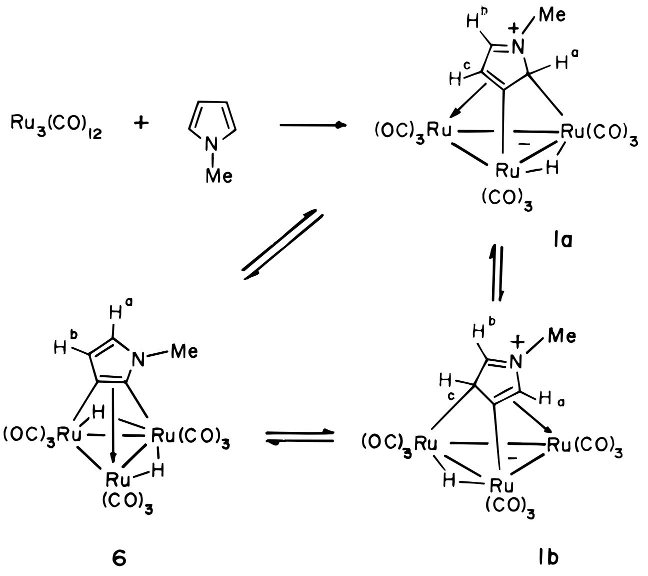


a different chemistry of pyrroles with ruthenium carbonyl clusters compared with that with osmium clusters. One feature of metal clusters containing pyrrole-derived ligands is the propensity for positive charge localization on the nitrogen atoms associated with a considerable electron drift away from the heterocycle toward the metal carbonyl cluster to give a zwitterionic system, resulting in lowering of the ν(CO) wavenumbers in the IR spectra. The formation of nonaromatic pyrrole- or indole-derived ligands is also an expected feature and commonly results when NH protons are present.[6,7] The range of methyl-substituted pyrroles that we have used in this present work imposes certain restraints: 1-methylpyrrole may be metalated at the 2- or 3-positions, whereas the pyrroles methylated at the 2- and 5-positions can only be ring-metalated at the 3-position. 1-Methylpyrrole and 1,2,5-trimethylpyrrole have no NH group to be metalated, whereas 2,5-dimethylpyrrole has. Therefore, the pyrroles we chose to study allow us to compare different aspects of their reactivity. In their initial reactions with $[Ru_3(CO)_{12}]$, they all give directly analogous compounds, except for the reaction of 2,5-dimethylpyrrole in toluene, which leads to both N−H and C−H bond cleavages at a methyl group instead of at the heterocyclic ring.

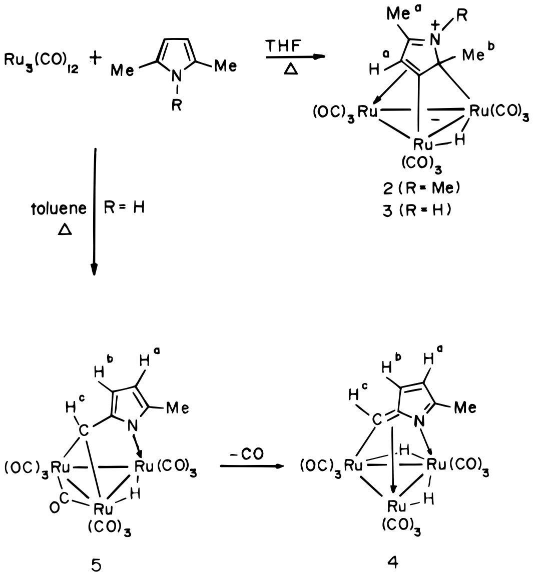
Results and Discussion

Reaction of 1-Methylpyrrole with $[Ru_3(CO)_{12}]$. The new clusters described in this report, **1**−**6**, are shown in Schemes 2 and 3. Reaction of $[Ru_3(CO)_{12}]$ with 1-methylpyrrole in refluxing octane for 2 h leads to a reaction mixture which was separated by TLC on silica to give one main band, which was isolated as yellow crystals of $[Ru_3(\mu\text{-H})(\mu_3,\eta^3\text{-}C_4H_3NMe)(CO)_9]$ (**1**). There was no evidence for a compound corresponding to the cluster $[Os_3(\mu\text{-H})(\mu,\eta^1\text{-}C_4H_3NMe)(CO)_{10}]$ obtained from $[Os_3(CO)_{10}(MeCN)_2]$ and 1-methylpyrrole; if such a ruthenium compound had been formed, it must have decarbonylated rapidly to cluster **1** under the reaction conditions.

Scheme 2



Scheme 3



The ^{1}H NMR spectrum of **1** shows broad resonances at room temperature, but at 260 K sharp resonances were assigned to two related isomeric compounds, **1a** and **1b**, [**1a**]/[**1b**] = 1.8 (Scheme 2). The major isomer **1a** shows five ^{1}H NMR resonances (Table 1) assigned to a metal hydride (δ −16.1), the NMe group (δ 3.60), and three CH groups of the ring (δ 8.39, 5.75, and 5.29). It is clear that metalation has occurred at a CH site of the ring, but the position of metalation could not be determined straightforwardly from these data. The minor isomer **1b** likewise shows a set of resonances that can be similarly assigned: hydride (δ −15.5), NMe (δ 3.75), and three CH ring protons (δ 8.51, 6.45, and 4.83). Above room temperature (313 K), coalescence to give a single set of five resonances occurs at chemical shifts consistent with pairwise coalescence of the 10 resonances with appropriate weighting observed at 260 K. Apart from the obvious coalescences of the pairs of NMe and hydride signals, the following pairwise coalescence occurred: δ 8.51 with 8.39, δ 6.45 with 5.29, and δ 4.83 with 5.75. The variable-temperature ^{1}H NMR spectra in CD_3COCD_3 are shown in Figure 1.

---

(4) (a) Arce, A. J.; Arrojo, P.; Deeming A. J.; De Sanctis, Y. *J. Chem. Soc., Dalton Trans.* **1992**, 2423. (b) Arce, A. J.; De Sanctis, Y.; Karam, A.; Deeming, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1381.

(5) (a) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, F. R. *Organometallics* **1988**, *7*, 1171. (b) Hüberer, P.; Weiss, E. *J. Organomet. Chem.* **1977**, *129*, 105.

(6) Arce, A. J.; De Sanctis Y.; Deeming, A. J. *J. Organomet. Chem.* **1986**, *311*, 371.

(7) Hardcastle, K. I.; Minassian, H.; Arce, A. J.; De Sanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1989**, *368*, 119.

Table 1. Spectroscopic Data for Compounds 1−6

compound	IR ν(CO)[a] (cm^{-1})	^{1}H NMR δ[b] (ppm)	*J* (Hz)
1, $[Ru_3(\mu\text{-}H)(\mu_3,\eta^3\text{-}C_4H_3NMe)(CO)_9]$	2082 m, 2053 s, 2027 vs, 2008 s, 1996 ms, 1986 ms, 1966 w	**1a** (major isomer):[c] 8.39 (s, H^a), 5.75 (s, H^c), 5.29 (s, H^b), 3.60 (s, Me), −16.1 (s, Ru−H) **1b** (minor isomer):[c] 8.51 (s, H^c), 6.45 (s, H^b), 4.83 (s, H^a), 3.75 (s, Me), −15.5 (s, Ru−H)	
2, $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^3\text{-}C_4H(Me)_2NMe\}(CO)_9]$	2080 m, 2050 s, 2024 vs, 2006 s, 1994 m, 1982 ms, 1966 w, 1955 w	4.86 (br s, H^a), 3.27 (s, Me^c), 2.06 (s, Me^b), 1.84 (br s, Me^a), −16.1 (br s, Ru−H)	
3, $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^3\text{-}C_4H(Me)_2NH\}(CO)_9]$	2079 m, 2049 s, 2023 vs, 2004 s, 1992 s, 1982 s, 1964 w, 1956 w	8.85 (br s, H^b),[d] 4.87 (br s, H^a), 2.17 (s, Me^b), 1.94 (br s, Me^a), −16.1 (br s, Ru−H)	
4, $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^2\text{-}CH{=}C_4H_2(Me)N\}(CO)_9]$	2092 m, 2065 s, 2037 vs, 2020 s, 2008 s, 1999 sh, 1982 w, 1976 w	8.52 (d, H^c), 7.45 (br d, H^a), 6.67 (d, H^b), 2.23 (d, Me), −16.2 (d, Ru−H)	H^{a}H^b = 4.7, H^{a}Me = 0.5, H^c(Ru−H) = 0.5
5, $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^2\text{-}CHC_4H_2(Me)N\}(\mu\text{-}CO)(CO)_9]$	2096 w, 2073 s, 2053 s, 2046 sh, 2038 s, 2026 w, 2013 vs, 1991 w, 1960 w, 1860 w	5.65 (d, H^a), 5.40 (d, H^c), 5.11 (d, H^b), 2.45 (s, Me), −15.2 (d, Ru−H)	H^{a}H^b = 2.6, H^c(Ru−H) = 0.6
6, $[Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}C_4H_2NMe)(CO)_9]$	2106 m, 2075 vs, 2053 vs, 2040 s, 2032 sh, 2027 m, 2009 vs, 1994 sh, 1986 m	6.37 (d, H^a), 6.06 (d, H^b), 3.54 (s, Me), −17.6 (s, 2Ru−H)	H^{a}H^b = 3.0

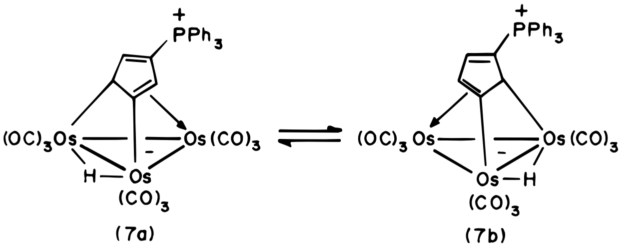
[a] In cyclohexane. [b] In $CDCl_3$, 300 MHz, 296 K. [c] In CD_3COCD_3 at 260 K. [d] In CD_2Cl_2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Ru_3(\mu\text{-}H)(\mu_3,\eta^3\text{-}C_4H_3NMe)(CO)_9]$ (1a)

Ru(1)−Ru(2)	2.7470(8)	Ru(3)−C(1)	2.264(5)
Ru(1)−Ru(3)	2.7871(9)	Ru(3)−H	1.87(6)
Ru(1)−C(2)	2.412(5)	C(1)−C(2)	1.440(7)
Ru(1)−C(3)	2.360(5)	C(1)−N(1)	1.425(6)
Ru(2)−Ru(3)	2.9244(9)	C(2)−C(3)	1.440(7)
Ru(2)−C(2)	2.063(5)	C(3)−C(4)	1.413(7)
Ru(2)−H	1.74(6)	C(4)−N(1)	1.292(7)

Ru(2)−Ru(1)−Ru(3)	63.79(2)	Ru(3)−C(1)−N(1)	118.2(3)
Ru(2)−Ru(1)−C(2)	46.59(11)	C(2)−C(1)−N(1)	106.0(4)
Ru(2)−Ru(1)−C(3)	76.48(13)	Ru(1)−C(2)−Ru(2)	75.3(2)
Ru(3)−Ru(1)−C(2)	58.64(11)	Ru(1)−C(2)−C(1)	117.0(3)
Ru(3)−Ru(1)−C(3)	85.82(13)	Ru(1)−C(2)−C(3)	70.4(3)
C(2)−Ru(1)−C(3)	35.1(2)	Ru(2)−C(2)−C(1)	123.6(3)
Ru(1)−Ru(2)−Ru(3)	58.77(2)	Ru(2)−C(2)−C(3)	129.2(4)
Ru(1)−Ru(2)−C(2)	58.14(13)	C(1)−C(2)−C(3)	105.3(4)
Ru(3)−Ru(2)−C(2)	58.97(13)	Ru(1)−C(3)−C(2)	74.5(3)
Ru(3)−Ru(2)−H	37(2)	Ru(1)−C(3)−C(4)	117.4(4)
Ru(1)−Ru(3)−Ru(2)	57.44(2)	C(2)−C(3)−C(4)	107.5(5)
Ru(1)−Ru(3)−C(1)	81.59(13)	C(3)−C(4)−N(1)	109.7(5)
Ru(2)−Ru(3)−C(1)	72.14(13)	C(4)−N(1)−C(1)	111.4(4)
Ru(3)−C(1)−C(2)	84.6(3)		

Scheme 4



An X-ray study was carried out on a single crystal obtained from a solution containing **1a**,**b**, revealing a molecular structure corresponding to isomer **1a**. The molecular structure is shown in Figure 2, and selected bond lengths and angles are listed in Table 2. The hydride ligand was located and refined appropiately, bridging the longest Ru−Ru edge [Ru(2)−Ru(3) = 2.9244(9) Å]. The Ru−H bond distances [Ru(2)−H = 1.74(6) and Ru(3)−H = 1.87(6) Å] compare well with the reported value [1.78(2) Å] for Ru−H bridging hydrides.[8] The organic ligand is essentially planar, the largest deviation of the mean least-squares plane of the heterocycle being 0.038(8) Å for the CH_3 carbon C(5). The 1-methylpyrrolyne ligand is clearly metalated at the 3-position to form the σ-bond Ru(2)−C(2) [2.063(5) Å], the atom Ru(2) lying close in the plane of the heterocycle [mean deviation from the plane, 0.4030(4) Å]. At first sight, the ligand appears to be a symmetrical η^3-bridge, but the detailed bond distances show that this is not the case.

Ru(3)−C(1) can be considered a σ-bond [2.264(5) Å], and C(2)−C(3) can be described as slightly asymmetrically η^2-coordinated to Ru(1) [Ru(1)−C(2) = 2.412(5) and Ru(1)−C(3) = 2.360(5) Å]; the mean least-squares plane of the heterocycle makes a dihedral angle of 41.8(1)° with the Ru_3 plane. An approximate description of the bonding is shown for **1a** in Scheme 2; the location of double bonds as shown requires a formal positive charge at the NMe group and negative charge at the metal atoms. The low values for the ν(CO) wavenumbers (three highest wavenumbers bands at 2082, 2053, and 2027 cm^{-1}) compared with values for related neutral Ru_3 clusters are consistent with a buildup of negative charge at the metal atoms. As an example of a non-zwitterionic complex, cluster **6** has the three highest wavenumber bands for ν(CO) at 2106, 2075, and 2053 cm^{-1} (Table 1). The ligand as a whole in **1a** is considered to be a five-electron donor with two σ-Ru−C bonds, one η^2-contact, and a negative charge, resulting from the zwitterionic description. This is a new type of heterocycle coordination, and the closest known cyclic analogue is observed in the structure of $[Os_3(\mu\text{-}H)(\mu_3,\eta^3\text{-}C_5H_2PPh_3)(CO)_9]$, which is clearly zwitterionic with an exocyclic phosphonium group and a very similar attachment of the C_5 ring to the M_3 triangle.[9] This exists as **7a** in the crystal but as two interconverting isomers, **7a** and **7b**, in solution (Scheme 4). Likewise, we propose that the dynamic behavior between **1a** and **1b** (Scheme 2) requires a hydride shift from one Ru−Ru edge to another and small geometric displacements of the ligand

---

(8) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(9) Deeming, A. J.; Powell, N. I.; Whittaker, C. *J. Chem. Soc., Dalton Trans.* **1991**, 1875.

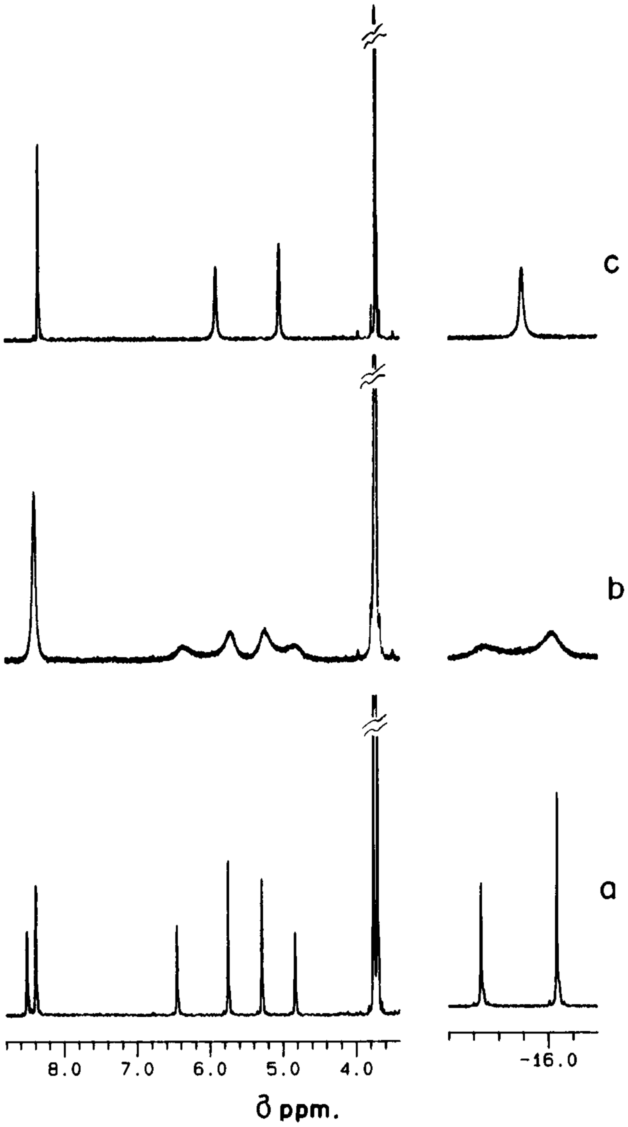


Figure 1. Variable-temperature ^{1}H NMR spectra of isomers **1a**,**b** in CD_3COCD_3: (a) 260, (b) 286, and (c) 313 K.

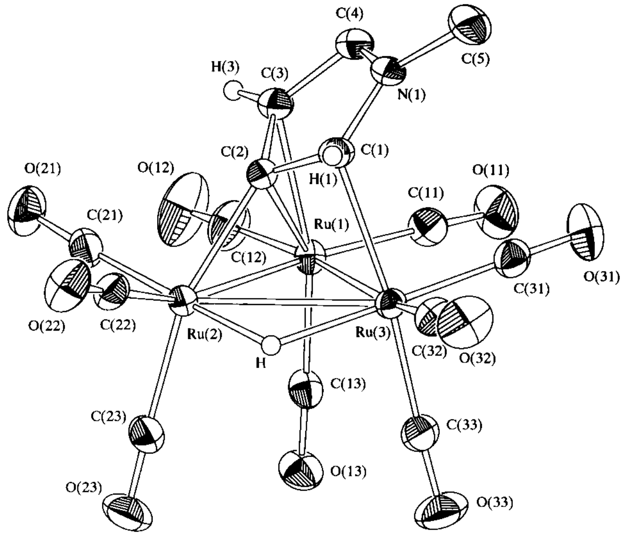


Figure 2. ORTEP drawing of **1a**, showing 35% probability thermal ellipsoids.

atoms position to interchange the σ-Ru−C and η^2-interactions. There is a related acyclic analogue, $[Ru_3(\mu\text{-}H)(\mu_3,\eta^3\text{-}CH_2{=}CC{=}NMe_2)(CO)_9]$, which likewise exists in a zwitterionic form and has the same distribution of η^1- and η^2-interactions between the ligand and the Ru_3 triangle.[10]

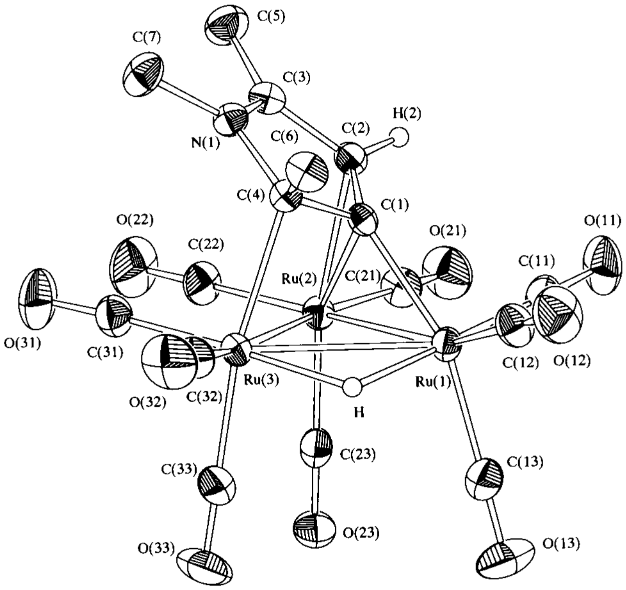


Figure 3. ORTEP drawing of **2**, showing 35% probability thermal ellipsoids.

There appears to be a pronounced solvent effect in the formation of clusters **1a** and **1b** rather than isomeric forms which are not zwitterionic. If a solution of **1a**,**b** in cyclohexane is heated under reflux, there is an esentially complete conversion to the nonzwitterionic isomer $[Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}C_4H_2NMe)(CO)_9]$ (**6**) which occurs by a β-elimination process. A hydrogen atom *ortho* to NMe has migrated to ruthenium to give the Ru analogue of the complex produced thermally from $[Os_3(CO)_{12}]$ and 1-methylpyrrole.[2,11] The ^{1}H NMR and IR spectra of **6** correspond to those of $[Os_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}C_4H_2NMe)(CO)_9]$, the X-ray structure of which has been determined.[11] This conversion of **1a**,**b** to **6** by a H atom transfer may be reversed in more polar solvents such as dichloromethane which favor the charge-separated species **1**.

Reactions of 1,2,5-Trimethylpyrrole and 2,5-Dimethylpyrrole with $[Ru_3(CO)_{12}]$. Related reactions of 1,2,5-trimethylpyrrole and 2,5-dimethylpyrrole with $[Ru_3(CO)_{12}]$ in refluxing THF give products directly corresponding to cluster **1**: $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^3\text{-}C_4H(Me)_2NMe\}(CO)_9]$ (**2**) and $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^3\text{-}C_4H(Me)_2NH\}(CO)_9]$ (**3**) (Scheme 3). Clusters **2** and **3** have IR ν(CO) and ^{1}H NMR spectra very similar to those of **1a** (Table 1), indicating that they are isostructural, but unlike for **1**, only a single isomer was observed in the NMR spectra, even at low temperatures. Either one isomer is not populated at low temperatures (which is more likely) or the process for **2** and **3** is much more rapid than that for the isomers **1a**,**b**. Molecular structures for **2** and **3** are shown in Figures 3 and 4, and selected bond lengths and angles are given in Tables 3 and 4, respectively. For **3**, there are two independent molecules in the asymmetric unit, and since there is very little difference between them, only one of these, molecule a, is illustrated.

---

[10] Aime, S.; Osella, D.; Arce, A. J.; Deeming, A. J.; Hursthouse, M. B.; Galas, A. M. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1981.

[11] Choo Yin, C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 2563.

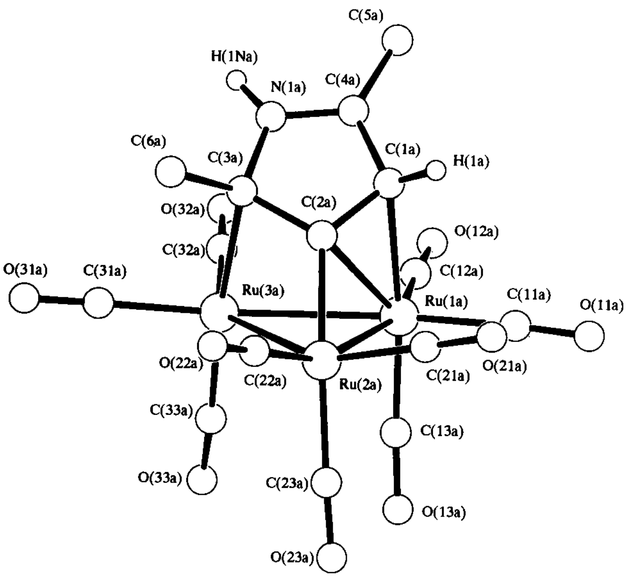
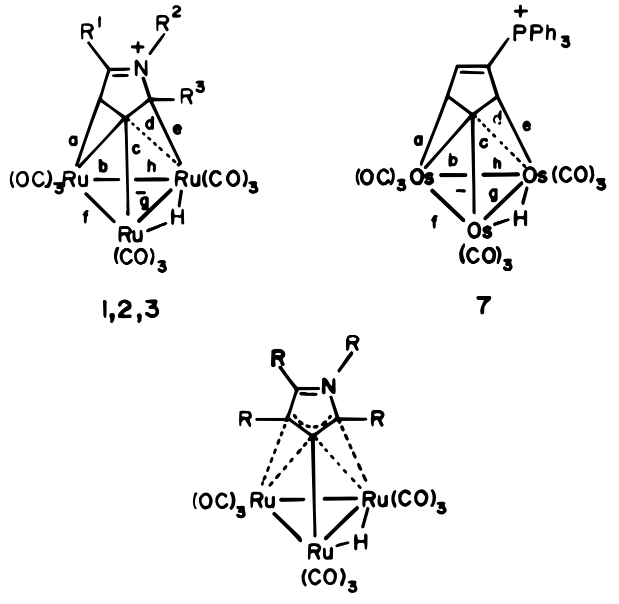


Figure 4. Molecular structure view of **3** (molecule a).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [$Ru_3(\mu$-H)$\{\mu_3,\eta^3$-$C_4H(Me)_2NMe\}(CO)_9$] (2)

Ru(1)–Ru(2)	2.7683(7)	Ru(3)–C(4)	2.244(6)
Ru(1)–Ru(3)	2.9356(5)	Ru(3)–H	1.82(6)
Ru(1)–C(1)	2.064(7)	C(1)–C(2)	1.439(10)
Ru(1)–H	1.80(5)	C(1)–C(4)	1.452(7)
Ru(2)–Ru(3)	2.8008(6)	C(2)–C(3)	1.445(8)
Ru(2)–C(1)	2.397(6)	N(1)–C(3)	1.274(7)
Ru(2)–C(2)	2.290(7)	N(1)–C(4)	1.468(8)
Ru(2)–Ru(1)–Ru(3)	58.73(2)	Ru(1)–C(1)–Ru(2)	76.31(13)
Ru(2)–Ru(1)–C(1)	57.3(2)	C(2)–C(1)–C(4)	107.5(4)
Ru(3)–Ru(1)–C(1)	58.49(10)	Ru(2)–C(2)–C(1)	76.2(3)
Ru(1)–Ru(2)–Ru(3)	63.62(2)	C(3)–C(2)–C(1)	106.2(5)
Ru(1)–Ru(2)–C(1)	46.41(12)	N(1)–C(3)–C(2)	110.3(5)
Ru(3)–Ru(2)–C(1)	58.35(13)	Ru(3)–C(4)–C(1)	84.7(3)
C(1)–Ru(2)–C(2)	35.7(2)	Ru(3)–C(4)–N(1)	115.4(4)
Ru(1)–Ru(3)–Ru(2)	57.65(2)	C(1)–C(4)–N(1)	103.7(4)
Ru(1)–Ru(3)–C(4)	72.38(10)	C(3)–N(1)–C(4)	112.3(5)

Chart 1



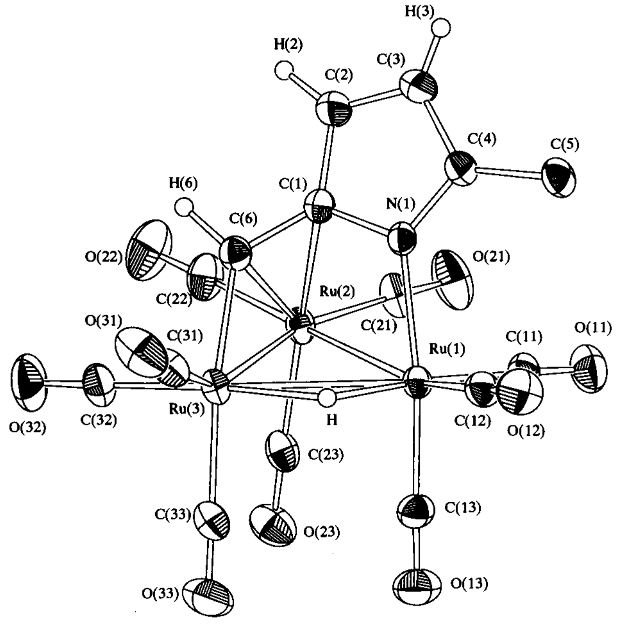


Figure 5. ORTEP drawing of **4**, showing 35% probability thermal ellipsoids.

Critical Ru–C and Ru–Ru distances for **1a**, **2**, and **3** (Chart 1) are compiled for direct comparison in Table 5, together with the corresponding distances Os–C and Os–Os for cluster **7a**. The bonding descriptions shown in Schemes 2 and 3 are certainly oversimplified. The three-carbon Ru-bonded group of atoms is much more closely symmetrical than implied in the schemes. Normally, Ru–C σ-bonds are around 2.06 Å, which is clearly the case for bond *c*, but the other supposedly σ-bond *e* is significantly longer (around 2.25 Å) and cannot be considered a pure σ-bond. The description given in Chart 1 with delocalized bonding is probably more accurate but cannot be simply represented.

Reaction of 2,5-Dimethylpyrrole with [$Ru_3(CO)_{12}$] with N–H and Methyl C–H Activation. If the reaction is carried out in toluene for 4 h, product **3** is not obtained, but the compounds [$Ru_3(\mu$-H)$\{\mu_3,\eta^3$-$CH{=}C_4H_2(Me)N\}(CO)_9$] (**4**, 15%) and [$Ru_3(\mu$-H)$\{\mu^3,\eta^2$-$CHC_4H_2(Me)N\}(\mu$-CO)$(CO)_9$] (**5**, 14%) are isolated instead. These compounds have been characterized spectroscopically (Table 1) and by X-ray analysis for **4**. The molecular structure of **4** is shown in Figure 5, and selected bond lengths and angles are given in Table 6. The crystal structure closely corresponds to the picture of **4** in Scheme 3. The ligand is N-bonded to ruthenium [Ru(1)–N(1), 2.096(4) Å]; metalation at the 1-position has left the pyrrole ring as an imine. There is a bond length alternation, with short double bonds at N(1)–C(4), C(2)–C(3), and C(1)–C(6). Thus, the exocyclic carbon is double bonded to the ring [C(1)–C(6) = 1.420(6) Å] and forms part of a μ,η^2-vinyl group bridging Ru(2) and Ru(3). Three hydrogen atoms have been abstracted from the original substituted pyrrole, one transfered to the ruthenium cluster and the other two presumably lost as H_2, although this has not been confirmed. The μ_3-ligand acts as a five-electron donor through the imine nitrogen N(1), a σ-bond, Ru(3)–C(6) [2.051(5) Å], and an η^2 interaction through C(1)–C(6) [Ru(2)–C(1) = 2.320(4) and Ru(2)–C(6) = 2.197(5) Å]. These bond lengths are as expected for this type of coordination.

Compound **4** is related to but distinctly different from other known nitrogen heterocyclic compounds in clusters with metalated exocyclic methyl groups. For example, 2-methylpyrrolidine reacts with [$Os_3(CO)_{10}$-$(MeCN)_2$] to activate either a ring C–H bond to give **8** or a C–H bond of the methyl group to give **9** (Scheme 5).[12] In this respect, there is similarity to the chemistry

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^3\text{-}C_4H(Me)_2NH\}(CO)_9]$ (3)

molecule a		molecule b	
Ru(1a)−Ru(2a)	2.746(2)	Ru(1b)−Ru(2b)	2.758(2)
Ru(1a)−Ru(3a)	2.790(2)	Ru(1b)−Ru(3b)	2.793(2)
Ru(1a)−C(1a)	2.34(2)	Ru(1b)−C(1b)	2.331(14)
Ru(1a)−C(2a)	2.36(2)	Ru(1b)−C(2b)	2.413(14)
Ru(2a)−Ru(3a)	2.935(2)	Ru(2b)−Ru(3b)	2.920(2)
Ru(2a)−C(2a)	2.048(14)	Ru(2b)−C(2b)	2.06(2)
Ru(3a)−C(3a)	2.26(2)	Ru(3b)−C(3b)	2.27(2)
C(1a)−C(2a)	1.40(2)	C(1b)−C(2b)	1.46(2)
C(1a)−C(4a)	1.43(2)	C(1b)−C(4b)	1.41(2)
C(2a)−C(3a)	1.47(2)	C(2b)−C(3b)	1.45(2)
C(4a)−C(5a)	1.50(2)	C(4b)−C(5b)	1.52(2)
C(3a)−N(1a)	1.44(2)	C(3b)−N(1b)	1.42(2)
C(4a)−N(1a)	1.28(2)	C(4b)−N(1b)	1.34(2)
Ru(2a)−Ru(1a)−Ru(3a)	64.03(5)	Ru(2b)−Ru(1b)−Ru(3b)	64.48(4)
Ru(2a)−Ru(1a)−C(2a)	46.5(4)	Ru(2b)−Ru(1b)−C(2b)	46.3(3)
C(1a)−Ru(1a)−C(2a)	34.5(6)	C(1b)−Ru(1b)−C(2b)	35.7(5)
Ru(1a)−Ru(2a)−Ru(3a)	58.71(4)	Ru(1b)−Ru(2b)−Ru(3b)	58.84(4)
Ru(1a)−Ru(2a)−C(2a)	56.9(4)	Ru(1b)−Ru(2b)−C(2b)	58.0(4)
Ru(3a)−Ru(2a)−C(2a)	58.2(4)	Ru(3b)−Ru(2b)−C(2b)	58.3(4)
Ru(1a)−Ru(3a)−Ru(2a)	57.26(4)	Ru(1b)−Ru(3b)−Ru(2b)	57.68(4)
Ru(1a)−Ru(3a)−C(3a)	82.3(4)	Ru(1b)−Ru(3b)−C(3b)	82.4(4)
Ru(1a)−C(1a)−C(2a)	73.7(9)	Ru(1b)−C(1b)−C(2b)	75.2(8)
C(2a)−C(1a)−C(4a)	109.5(14)	C(2b)−C(1b)−C(4b)	107.2(14)
Ru(1a)−C(2a)−Ru(2a)	76.6(5)	Ru(1b)−C(2b)−Ru(2b)	75.7(5)
Ru(1a)−C(2a)−C(1a)	71.8(10)	Ru(1b)−C(2b)−C(1b)	69.1(8)
Ru(1a)−C(2a)−C(3a)	120.1(10)	Ru(1b)−C(2b)−C(3b)	118.9(10)
C(1a)−C(2a)−C(3a)	105.7(12)	C(1b)−C(2b)−C(3b)	106.7(13)
C(2a)−C(3a)−N(1a)	103.9(12)	C(2b)−C(3b)−N(1b)	105.2(13)
C(1a)−C(4a)−N(1a)	107.6(14)	C(1b)−C(4b)−N(1b)	109.1(13)
C(3a)−N(1a)−C(4a)	113.2(13)	C(3b)−N(1b)−C(4b)	111.8(13)

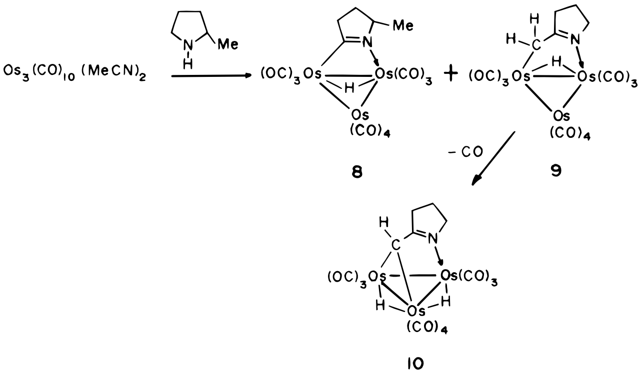
Table 5. Comparative Bond Length Data (Å) for Structures 1a, 2, 3, and 7a

	1a	2	3	7a
R^1	H	Me	H	
R^2	Me	Me	Me	
R^3	Me	H	Me	
a	2.355(6)	2.290(4)	2.34(2)	2.36(1)
b	2.404(5)	2.397(6)	2.36(2)	2.45(1)
c	2.064(5)	2.064(4)	2.05(2)	2.11(1)
d	2.567(5)	2.558(4)	2.34(2)	2.63(1)
e	2.257(5)	2.244(3)	2.25(2)	2.27(1)
f	2.7476(8)	2.7685(7)	2.746(2)	2.782(1)
g	2.9250(9)	2.9358(4)	2.935(2)	2.957(1)
h	2.7872(9)	2.8010(7)	2.790(2)	2.838(1)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^2\text{-}CH{=}C_4H_2(Me)N\}(CO)_9]$ (4)

Ru(1)−Ru(2)	2.7941(6)	Ru(3)−H	1.85(6)
Ru(1)−Ru(3)	2.9621(7)	C(1)−C(2)	1.450(7)
Ru(1)−N(1)	2.096(4)	C(1)−C(6)	1.420(7)
Ru(1)−H	1.74(6)	C(1)−N(1)	1.423(6)
Ru(2)−Ru(3)	2.7559(8)	C(2)−C(3)	1.340(8)
Ru(2)−C(1)	2.320(4)	C(3)−C(4)	1.440(7)
Ru(2)−C(6)	2.197(4)	C(4)−C(5)	1.493(8)
Ru(3)−C(6)	2.051(5)	C(4)−N(1)	1.325(6)
Ru(2)−Ru(1)−Ru(3)	57.12(4)	Ru(2)−C(1)−N(1)	97.0(3)
Ru(2)−Ru(1)−N(1)	70.13(10)	C(2)−C(1)−C(6)	128.1(5)
Ru(3)−Ru(1)−N(1)	84.00(10)	C(2)−C(1)−N(1)	106.9(4)
Ru(1)−Ru(2)−Ru(3)	64.51(2)	C(6)−C(1)−N(1)	121.7(4)
Ru(1)−Ru(2)−C(1)	70.56(11)	C(1)−C(2)−C(3)	107.3(5)
Ru(1)−Ru(2)−C(6)	81.06(12)	C(2)−C(3)−C(4)	108.3(5)
Ru(3)−Ru(2)−C(1)	75.60(12)	C(3)−C(4)−N(1)	109.7(4)
Ru(3)−Ru(2)−C(6)	47.29(13)	Ru(2)−C(6)−Ru(3)	80.8(2)
C(1)−Ru(2)−C(6)	36.5(2)	Ru(2)−C(6)−C(1)	76.5(3)
Ru(1)−Ru(3)−Ru(2)	58.37(2)	Ru(3)−C(6)−C(1)	127.8(4)
Ru(1)−Ru(3)−C(6)	79.31(13)	Ru(1)−N(1)−C(1)	114.3(3)
Ru(2)−Ru(3)−C(6)	51.91(13)	Ru(1)−N(1)−C(4)	133.8(3)
Ru(2)−C(1)−C(2)	126.7(3)	C(1)−N(1)−C(4)	107.9(4)
Ru(2)−C(1)−C(6)	67.0(3)		

Scheme 5



of methyl-substituted pyrroles described here. Decarbonylation of **8** leads to a second metalation of the methyl group (as in the formation of **4**), but the product $[Os_3(\mu\text{-}H)_2(\mu^3,\eta^2\text{-}CHC_4H_6N)(CO)_9]$ (**10**) has an sp^3 rather than an sp^2 exocyclic CH group. In principle, cluster **4** is a dehydrogenated form of a cluster like **10**, except for the different metal centers and the different substitution at the ring.

The other product from this reaction, **5**, contains a μ_3-ligand stoichiometrically equivalent to that of **4**, but the NMR spectra show that is very differently coordinated. The exocyclic CH ^{1}H NMR signal has shifted upfield from δ 8.52 in **4** to δ 5.40 in **5**, consistent with the representation shown in Scheme 3, in which the exocyclic CH acts as an alkylidene bridge. The change of the μ_3-ligand from a five-electron donor in **4** to a three-electron donor in **5** is, of course, compatible with the presence of an extra CO ligand. The extra CO ligand is bridging; the IR spectrum of **5** reveals a ν(CO) absorption at 1860 cm^{-1}. The structure **5** in Scheme 3 is consistent with these data, but we cannot be certain of the relative position of the μ-H, μ-CO, and μ_3-ligand.

---

(12) Day, M.; Freeman, W.; Hardcastle, K. I.; Isomaki, M.; Kabir, S. E.; McPhillips, T.; Rosenberg, E.; Scott, L. G.; Wolf, E. *Organometallics* **1992**, *11*, 3376.

Table 7. Crystallographic Data for Compounds 1−4

	1	**2**	**3**	**4**
formula	$C_{14}H_7NO_9Ru_3$	$C_{16}H_{11}NO_9Ru_3$	$C_{15}H_9NO_9Ru_3$	$C_{15}H_7NO_9Ru_3$
fw	636.42	664.47	650.44	648.43
cryst size, mm	0.20 × 0.16 × 0.10	0.48 × 0.32 × 0.12	0.30 × 0.26 × 0.23	0.30 × 0.26 × 0.15
symmetry	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	monoclinic, *Cc*	monoclinic, $P2_1/n$
a, Å	9.537(3)	9.021(2)	9.715(3)	9.375(2)
b, Å	11.386(3)	15.8172(9)	16.314(3)	19.875(2)
c, Å	17.680(3)	15.130(3)	25.105(3)	11.0687(14)
β, deg	92.88(2)	107.105(4)	96.450(14)	107.230(13)
V, Å^3	1917.4(8)	2063.3(6)	3953.7(13)	1969.9(5)
Z	4	4	8	4
ρ_{calcd}, g cm^{-3}	2.205	2.139	2.185	2.186
F(000)	1208	1272	2480	1232
μ(Mo Kα), cm^{-1}	23.8	22.2	23.1	23.2
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å) with graphite-oriented monochromator			
collection mode/range	$\omega-2\theta$ ($3 \leq 2\theta \leq 50°$)			
no. of total rflns	3593	7919	4969	3697
unique/*R*(int)	3378/0.0235	1969/0.0186	2377/0.026	3475/0.0154
obsd [$I > 2\sigma(I)$]	2852	1847	2167	3141
min/max transm	0.910^a/1.1.21^a	0.679/1.000	0.911/1.000	0.712/1.000
R1;^{b} wR2^c [$I > 2\sigma(I)$]	0.0339; 0.0923	0.0209; 0.0580	0.0320; 0.0686	0.0347; 0.0900
R1;^{b} wR2^c (all data)	0.0448; 0.1040	0.0324; 0.0941	0.0391; 0.0722	0.0388; 0.0964
g_1;^{c} g_2^{c}	0.0677; 1.27	0.0409; 0.81	0.0343; 19.10	0.0658; 1.50
goodness of fit^d on F^2	1.042	1.006	1.042	1.062
data-to-parameters ratio	12.9:1	7.4:1	7.3:1	13.5:1
final max/min $\Delta\rho$, e Å^{-3}	2.13/−0.508	0.291/−0.356	0.578/−0.427	1.045/−1.075

[a] These values correspond to minimum and maximum correction factors. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (x_1P)^2 + x_2P]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [d] $[\sum w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{params})]^{1/2}$.

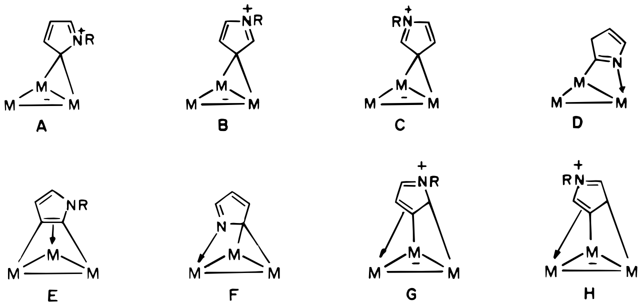


Figure 6. Established modes of coordination of pyrrole-derived ligands in triruthenium and triosmium clusters.

We think it is likely that the μ-CO and the μ-alkylidene will bridge the same two Ru atoms, which will be associated with a short Ru−Ru distance. In the absence of crystals of suitable quality for structure determination, these proposals cannot be substantiated.

There is now a considerable range of known organonitrogen ligands that μ_3-coordinate in triruthenium and triosmium clusters.[12−14] These fall into two broad categories: (A) those that are N-coordinated and (B) those that are only coordinated through carbon atoms. Commonly, the free nitrogen atom in the latter case is sp^2 hybridized, making a zwitterionic description of the cluster appropriate.

Figure 6 shows the range of simple ruthenium or osmium cluster derivatives that have been derived from pyrrole. The μ_2-forms **A**−**C** are observed in the zwitterionic alkylidene systems $[M_3(\mu\text{-H})(\mu\text{-L})(CO)_{10}]$.[1] When R = H rather than Me, other tautomeric forms are accessible, such as **D** as found in $[Os_3(\mu\text{-H})(\mu\text{-}C_4H_4N)(CO)_{10}]$.[6,15] In the decacarbonyl complexes, the neutral ligand formally donates three electrons, whereas in the decarbonylated forms **E**−**H** in the clusters $[M_3(\mu\text{-H})_x(\mu_3\text{-L})(CO)_9]$, four ($x = 2$) or five ($x = 1$) electrons are donated. The 2,3-pyrrolyne ligand **E** relates closely to other alkyne or aryne clusters,[2] but forms **F**−**H** are unique to pyrrole derivatives. As with **D**, form **F** is only easily available from pyrroles retaining NH groups.[6,15] In this article, we have described the new types of coordination, **G** and **H**. Finally, the ligand system **D** can be formally deprotonated and η^5-coordinated to another metal atom (Fe or Mn), although in practice complexes such as $[Os_3(\mu\text{-H})\{\mu\text{-}(C_4H_3N)ML_n\}(CO)_{10}]$ $\{ML_n$ = FeCp or $Mn(CO)_3\}$ are formed from azaferrocene or $[Mn(\eta^5\text{-}C_5H_4N)(CO)_3]$ by oxidative addition at triosmium clusters.[16]

Experimental Section

All the reactions were carried out under a nitrogen atmosphere. Solvents were purified by standard methods and distilled prior to use. $[Ru_3(CO)_{12}]$, 1-methylpyrrole, 2,5-dimethylpyrrole, and 1,2,5-trimethylpyrrole were purchased from Aldrich.

Synthesis of $[Ru_3(\mu\text{-H})(\mu_3,\eta^3\text{-}C_4H_3NMe)(CO)_9]$ (1). One hundred milligrams of $[Ru_3(CO)_{12}]$ (0.16 mmol) was dissolved in refluxing *n*-octane (40 mL), and then 0.7 mL of 1-methylpyrrole (8 mmol) was added to the refluxing solution. The reaction was stopped after 2 h, after which time there were no more changes in the IR spectra. The solvent was removed under vacuum, and the orange-brown residue was purified by TLC (SiO_2, eluant *n*-hexane/CH_2Cl_2 3/1), yielding 20 mg (19%) of **1** as yellow crystals from cyclohexane.

Thermal Treatment of 1. Fifteen milligrams of cluster **1** was dissolved in 30 mL of cyclohexane, and the solution was taken to reflux for 2 h. After TLC separation (*n*-hexane), only

---

(13) (a) Day, M.; Espitia, D.; Hardcastle, K. I.; Kabir, S. E.; Rosenberg, E.; Gobetto, R.; Milone, L.; Osella, D. *Organometallics* **1991**, *10*, 3550. (b) Day, M.; Hajela, S.; Kabir, S. E.; Irving, M.; McPhillips, T.; Wolf, E.; Hardcastle, K. I.; Rosenberg, E.; Milone, L.; Gobetto, R.; Osella, D. *Organometallics* **1991**, *10*, 2743.

(14) (a) Kabir, S. E.; Rosenberg, E.; Day, M.; Hardcastle, K. I.; Wolf, E; McPhillips, T. *Organometallics* **1995**, *14*, 721. (b) Kabir, S. E.; Kolwaite, D. S.; Rosenberg, E.; Scott, L. G.; McPhillips, T.; Duque, R.; Day, M.; Hardcastle, K. I. *Organometallics* **1996**, *15*, 1979.

(15) Day, M.; Hardcastle, K.; Deeming, A. J.; Arce, A. J.; De Sanctis, Y. *Organometallics* **1990**, *9*, 6.

(16) (a) Arce, A. J.; Acuña, C; Deeming, A. J. *J. Organomet. Chem.* **1988**, *356*, C47. (b) Best, S. P.; Clark, R. J. H.; Deeming, A. J.; McQueen, R. C. S.; Powell, N. I.; Acuña, C.; Arce, A. J.; De Sanctis, Y. *J. Chem. Soc., Dalton Trans.* **1991**, 1111.

one product was isolated, $[Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}C_4H_2NMe)(CO)_9]$ (**6**), as a pale yellow solid (8 mg, 50%).

Synthesis of $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^3\text{-}C_4H(Me)_2NMe\}(CO)_9]$ (2). One hundred milligrams of $[Ru_3(CO)_{12}]$ (0.16 mmol) was dissolved in 50 mL of dry THF, and then 0.5 mL of 1,2,5-trimethylpyrrole (3.8 mmol) was added to the refluxing solution. The reaction was stopped after 24 h. The solvent was removed under vacuum, and TLC separation (SiO_2, *n*-hexane) gave **2** (17 mg, 16%) as yellow crystals from cyclohexane. Carrying out the reaction in CH_2Cl_2 or toluene gave the same result.

Synthesis of $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^3\text{-}C_4H(Me)_2NH\}(CO)_9]$ (3). One hundred milligrams of $[Ru_3(CO)_{12}]$ (0.16 mmol) was dissolved in 50 mL of dry THF, and then 0.5 mL of 2,5-dimethylpyrrole (4.8 mmol) was added to the refluxing solution. The reaction was followed by changes in the IR spectrum, and the reaction was stopped after 16 h. TLC separation (SiO_2, eluant light petroleum/CH_2Cl_2 4/1) gave **3** (22 mg, 21%) as yellow crystals from cyclohexane.

Synthesis of $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^3\text{-}CH{=}C_4H_2(Me)N\}(CO)_9]$ (4) and $[Ru_3(\mu\text{-}H)\{\mu_3,\eta^2\text{-}CHC_4H_2(Me)N\}(\mu\text{-}CO)(CO)_9]$ (5). To a refluxing solution of $[Ru_3(CO)_{12}]$ (110 mg, 0.18 mmol) in 50 mL of toluene was added 0.6 mL (5.8 mmol) of 2,5-dimethylpyrrole. The reaction was stopped after 4 h, after which time there were no further changes in the IR spectra. TLC separation (SiO_2, eluant *n*-hexane/CH_2Cl_2 4/1) gave **4** (18 mg, 15%) as red crystals from cyclohexane and **5** (17 mg, 14%) as a yellow solid.

Crystal Structure Determinations for Clusters 1−4. Crystal data and selected experimental details are given in Table 7. Intensity data were collected at room temperature by use of a Rigaku AFC7S four-cycle automated diffractometer with graphite-monochromatized Mo Kα radiation. Data reduction and graphical representations were done by using the teXsan[17] package. Lorentz and polarization corrections were applied. Data for **2**−**4** were corrected for absorption by using the semiempirical method[18] based on several azimuthal scans, while for complex **1** an empirical method[19] was used.

All crystal structures were solved by direct methods (SIR92)[20] and Fourier techniques. Refinement was done by full-matrix least-squares calculations using SHELXL-93.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters, except for **3**, where atoms of the carbonyl groups were refined with isotropic displacement parameters. The Flack parameter,[22] $x = -0.03(7)$, was calculated in order to establish the absolute structure of **3**. In each case, the hydrogen atoms were included in calculated (C−H = 0.98 Å) and found positions using a riding model with a common isotropic displacement parameter. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[23]

In the last cycle of refinement of the crystal structures of **1**, **2**, and **4**, one peak of electronic density appropriate for the hydride atom bridging the longest Ru−Ru triangle edge was located from the difference Fourier map. Each peak was included, and their coordinates and thermal isotropic parameters were observed to refine in consistent form.

Acknowledgment. We thank Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT) of Venezuela, Project S1-95000578 and travel grant to UCL (Y.D.S.); the British Council for support of this collaboration between the UCL and IVIC groups; and CONICYT (Chile).

Supporting Information Available: Experimental details for the X-ray structure determinations and tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, and anisotropic displacement parameters for compounds **1**−**4** (87 pages). See any current masthead page for ordering information.

OM960847X

---

[17] *teXsan, Structure Analysis Software*; Molecular Structure Corp.: The Woodlands, TX, 1995.

[18] North, A. T. C.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

[19] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 159.

[20] *SIR92*: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[21] Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Götingen: Göttingen, Germany, 1993.

[22] Bernardinelli, G.; Flack, H. D. *Acta Crystallogr., Sect. A* **1985**, *41*, 500.

[23] Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.