Polynuclear η²-Benzophenone Methylhydrazonato(1−) Complexes from the Insertion of Ph₂CN₂ into Ti–CH₃ Bonds of Electron-Deficient Organotitanium Oxides. X-ray Structure of [Ti(C₅Me₅)Me(η²-MeNNCPh₂)][Ti(C₅Me₅)Me₂](μ-O)

Ricardo Serrano, Juan Carlos Flores, Pascual Royo,* and Miguel Mena

Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, Alcalá de Henares, 28871 Madrid, Spain

Maria Angela Pellinghelli and Antonio Tiripicchio

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

Ph₂CN₂ reacts stepwise with (TiCp*Me₂)₂(μ-O) to give first [TiCp*Me(η²-MeNNCPh₂)][TiCp*Me₂](μ-O) (3) and then [TiCp*Me(η²-MeNNCPh₂)]₂(μ-O) (4) containing benzophenone methylhydrazonato(1−) groups that are the insertion products of the diphenyldiazomethane into a Ti–Me bond of one or both metal centers, respectively. With [TiCp*Me(μ-O)]₃ insertion of Ph₂CN₂ into only one of the three Ti–Me bonds takes place. The structure of 3 has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/n$, with unit cell parameters $a = 19.372$ (4) Å, $b = 20.155$ (8) Å, $c = 9.081$ (2) Å, $\beta = 95.13$ (2)°, and $Z = 4$. The structure of 3 shows the hydrazonato(1−) ligand coordinated to one Ti atom in a η² fashion and the Ti–O–Ti bond angle departing ca. 20° from linearity.

Introduction

We have recently described[1] the di- and trinuclear organotitanium oxides [Cp*Me₂Ti]₂(μ-O) (1) and [Cp*Me(μ-O)Ti]₃ (2) and wanted to study the reactivity of these electron-deficient metal centers connected by oxo groups. In this paper we report the results of their reactions with Ph₂CN₂ leading to di- or trinuclear η²-hydrazonato complexes.

Diazoalkanes coordinate to transition metals in a variety of modes.[2] They are also synthetically useful reagents through N₂ elimination, and the additions of carbene fragments to multiple bonds between transition-metal atoms[3] or between atoms of transition and main group elements[4] are well-known processes. The insertion of diazoalkanes into transition-metal–hydrogen or –carbon bonds is a rare process that more usually can be described as a 1,3-addition to give diazenido complexes[5] while there are only a few reports of a 1,2-addition to give hydrazonato(1−) complexes.[6]

Results and Discussion

When a solution of Ph₂CN₂ in hexane is added dropwise to 1 at −45 °C in the same solvent, the red-violet color of the diphenyldiazomethane disappears immediately and a

Scheme I
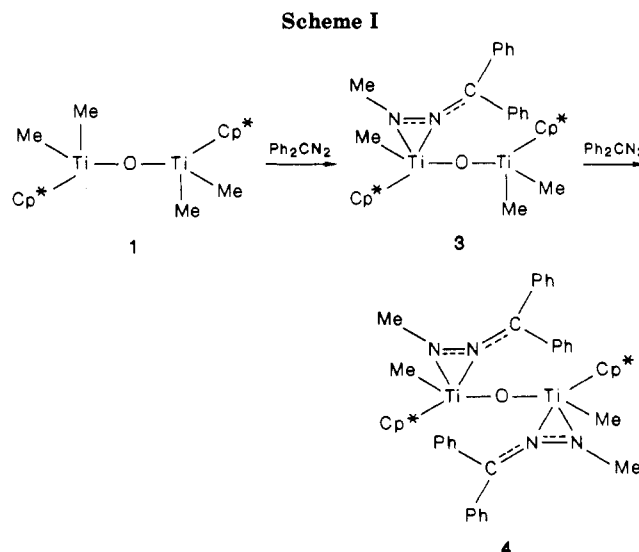
yellow precipitate is formed; after addition of 1 mol of Ph₂CN₂/mol of dimer 1, compound 3 is isolated simply by filtration. Its ¹H NMR spectrum clearly shows the presence of two nonequivalent metal fragments that give rise to two Cp* signals (δ 2.04 and 1.89 in C₆D₆) and two sets of Ti-bonded methyls (δ 0.79, 0.76, and 0.60 in C₆D₆); at the same time, the transfer of one CH₃ from Ti to nitrogen is evidenced by the shift of its signal to lower field (δ 2.83 in C₆D₆). The ratio is 15:15:6:3:3. It is easy to infer then that insertion of one Ph₂CN₂ molecule into one of the four original TiMe groups has taken place, giving rise to a hydrazonato(1−) group. The ¹³C{¹H} spectrum is in agreement with the proton spectrum and additionally shows that both phenyl rings are nonequivalent as eight peaks are observed.

When a second mole of Ph₂CN₂ is added to 3, or alternatively, 2 mol of Ph₂CN₂ are added to 1, a second diphenyldiazomethane molecule inserts into a Ti–Me bond of the other metal center producing 4 (Scheme I) that, according to its ¹H NMR spectrum, is a symmetrical species showing only one peak for every type of methyl

(1) García-Blanco, S.; Gómez Sal, M. P.; Martínez Carreras, S.; Mena, M.; Royo, P.; Serrano, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1572.
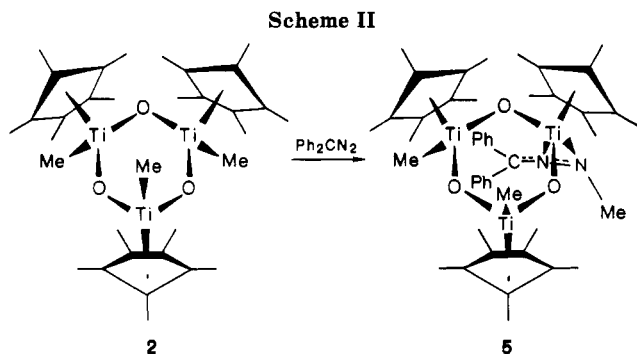
(2) See for example: (a) Nucciarone, D.; Taylor, N. J.; Carthy, A. J. *Organometallics* **1986**, *5*, 2565. (b) Curtis, M. D.; Messerlee, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283 and references therein.

(3) For review see: Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

(4) (a) Herrmann, W. A.; Weichmann, J.; Serrano, R.; Blechschmidtt, K.; Pfisterer, H.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 314. (c) Herrmann, W. A.; Weichmann, J.; Küsthardt, U.; Schäfer, A.; Hörlein, R.; Hecht, C.; Voss, E.; Serrano, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 979.

(5) (a) Herrmann, W. A.; Biersack, H.; Mayer, K. K.; Reuter, B. *Chem. Ber.* **1980**, *113*, 2655. (b) Lappert, M. F.; Poland, J. S. *J. Chem. Soc., Chem. Commun.* **1969**, 1061 and references therein.

(6) (a) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 263. (b) Gambarotta, S.; Floriani, C.; Chiesi Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029.

Scheme II

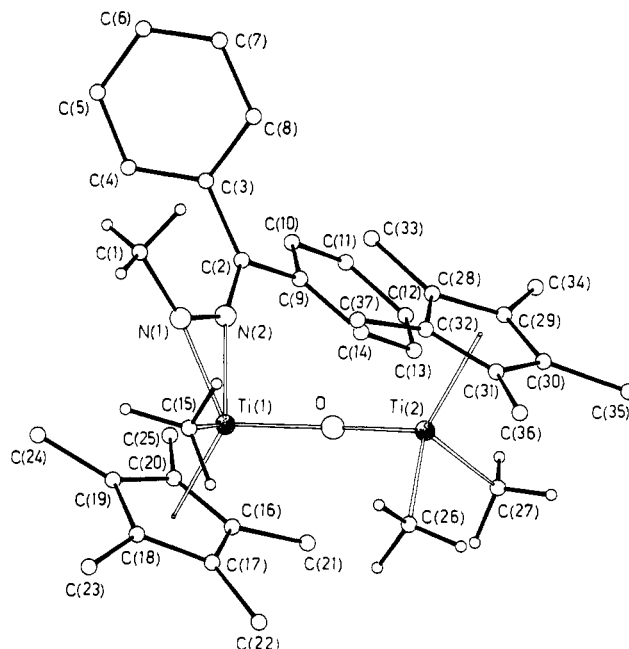**Figure 1.** View of the structure of **3** with the atomic numbering scheme.

group: N–Me (δ 2.65), C_5Me_5 (δ 1.96), and Ti–Me (δ 1.01) in the ratio 6:30:6. The $^{13}C\{^1H\}$ NMR spectrum also shows one peak for every type of methyl group and penta-methylcyclopentadienyl ring carbons but shows 12 signals for the phenyl ring carbon atoms, indicating that there is no free rotation around the C–Ph bonds at room temperature so that all the ring C atoms within each CPh_2 moiety are chemically unequivalent. The molecule must possess a center of symmetry, as noted earlier, so that 12 and not 24 peaks are seen.

No further insertion of Ph_2CN_2 into the remaining two Ti–Me bonds of **4** takes place when an excess of diphenyldiazomethane is used. Moreover, when 1 mol of Ph_2CN_2 is added to **1** at room temperature, a mixture of **3** and **4**, along with unreacted **1**, is obtained, indicating that the "nonreacted" Ti atom of **3** remains as unsaturated and reactive as it was in **1** and that it tends to insert a diphenyldiazomethane molecule in competition to **1**. The reaction between Ph_2CN_2 and the trimer **2** is considerably more difficult and proceeds only upon heating, according to Scheme II. This is in agreement with our general observation that substitution of one methyl group in **1** by one oxygen atom, a hard base, to give **2** renders the titanium center considerably less reactive. Even with an excess of Ph_2CN_2 the insertion in only one of the three Ti–Me bonds is observed. The structure of **3**, commented on below, and that of the starting product **2** can help us to understand the above result and the probable nature of the reaction product **5**. It has been reported[1] elsewhere that the three Cp*Me(μ-O)Ti units of **2** are linked, forming an almost planar Ti_3O_3 six-membered ring with two Cp* groups and one titanium-bonded CH_3 situated above the plane, while the other Cp* and two methyls lie below it. The reaction probably involves one of the two Ti–CH_3 bonds situated "below", at the less crowded side.

The ^1H NMR spectrum of **5** in THF-d_8 shows one peak for every Cp* group and two Ti–Me peaks. The rigidity of the phenyl groups is again indicated by the observation of 12 peaks in the $^{13}C\{^1H\}$ NMR spectrum. The crowding originated at both sides of the Ti_3O_3 ring by the bulky Cp* groups and phenyl rings should prevent further insertions from taking place.

Remarkable features in the IR spectra of **3**, **4**, and **5** are the ν(TiOTi) broad and intense bands at 780–725 cm^{-1} evidencing the preservation of the oxygen-bridged polynuclear systems and the ν(CN) band at 1530–1515 cm^{-1} indicative of a partial multiple character of the Ph_2C–N_2 bond.[6b]

Crystal Structure of 3. The exact coordination mode of the benzophenone methylhydrazonato(1–) ligand in these complexes has been fully elucidated by the X-ray structure determination of **3**. The structure of **3** is depicted in Figure 1; a list of important distances and angles is given in Table I and a list of some interplanar angles in Table SI.

Table I. Important Interatomic Distances (Å) and Angles (deg) for 3^a

Bond Distances			
Ti(1)–O	1.861 (5)	Ti(2)–C(27)	2.107 (12)
Ti(1)–N(1)	1.949 (6)	Ti(2)–CE(2)	2.074 (9)
Ti(1)–N(2)	2.118 (6)	N(1)–N(2)	1.326 (10)
T(1)–C(15)	2.141 (10)	N(1)–C(1)	1.442 (12)
Ti(1)–CE(1)	2.062 (10)	N(2)–C(2)	1.298 (10)
Ti(2)–O	1.788 (5)	C(2)–C(3)	1.486 (10)
Ti(2)–C(26)	2.094 (10)	C(2)–C(9)	1.492 (11)

Bond Angles			
C(15)–Ti(1)–CE(1)	109.2 (4)	O–Ti(2)–C(26)	103.2 (3)
N(2)–Ti(1)–CE(1)	114.1 (4)	Ti(1)–O–Ti(2)	161.9 (3)
N(2)–Ti(1)–C(15)	120.3 (3)	Ti(1)–N(1)–C(1)	155.5 (6)
N(1)–Ti(1)–CE(1)	122.4 (4)	Ti(1)–N(1)–N(2)	78.0 (4)
N(1)–Ti(1)–C(15)	84.4 (3)	N(2)–N(1)–C(1)	125.5 (7)
N(1)–Ti(1)–N(2)	37.8 (3)	Ti(1)–N(2)–N(1)	64.2 (4)
O–Ti(1)–CE(1)	119.7 (4)	N(1)–N(2)–C(2)	133.1 (7)
O–Ti(1)–C(15)	95.5 (3)	Ti(1)–N(2)–C(2)	162.6 (6)
O–Ti(1)–N(2)	96.8 (2)	N(2)–C(2)–C(9)	117.2 (7)
O–Ti(1)–N(1)	113.8 (3)	N(2)–C(2)–C(3)	124.8 (7)
C(27)–Ti(2)–CE(2)	111.9 (4)	C(3)–C(2)–C(9)	118.0 (6)
C(26)–Ti(2)–CE(2)	112.4 (4)	C(2)–C(3)–C(8)	118.5 (7)
C(26)–Ti(2)–C(27)	99.2 (5)	C(2)–C(3)–C(4)	122.9 (7)
O–Ti(2)–CE(2)	125.0 (3)	C(2)–C(9)–C(14)	122.3 (7)
O–Ti(2)–C(27)	101.6 (4)	C(2)–C(9)–C(10)	119.1 (7)

^{a} Estimated standard deviations are given in parentheses. CE(1) and CE(2) are the centroids of the C(16)···C(20) and C(28)···C(32) rings, respectively.

The hydrazonato(1–) ligand is bonded in an asymmetric η^2 fashion to one of the Ti atoms [Ti(1)–N(1) = 1.949 (6) and Ti(1)–N(2) = 2.118 (6) Å] in such a way that one of the phenyl rings of the diphenylcarbene moiety points on the side of the second Ti atom, whose Cp* ring lies almost parallel to it [dihedral angle 13.4 (3)°] in order to avoid interatomic repulsions. Nevertheless, this situation seems to force the tilting of the Cp*Me_2Ti(2) fragment so that the Ti(1)–O–Ti(2) angle shows a value of 161.9 (3)° which is, to our knowledge, the lowest so far reported for a M_2O-type dimeric compound of a d^0 early transition metal, whose tendency to form linear M–O–M bonds is known.[7]

(7) Petersen, J. L. *J. Organomet. Chem.* **1979**, *166*, 179.
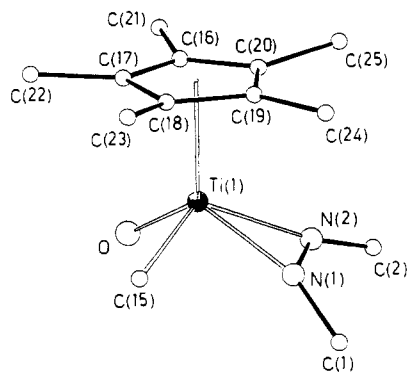
Figure 2. View of the coordination environment of the Ti(1) atom.

The distances from the titanium atoms to the pentamethylcyclopentadienyl rings, the methyl groups, and the oxygen bridging atom are usual in this type of compounds.[8] The greater electronic insaturation of Ti(2) with respect to Ti(1) results in shorter Ti–Me and Ti–O distances for Ti(2), the differences in bond lengths being 0.03–0.05 and 0.07 Å, respectively, although the different degree of ligand crowding around the metal atoms could also have some effects on these values.
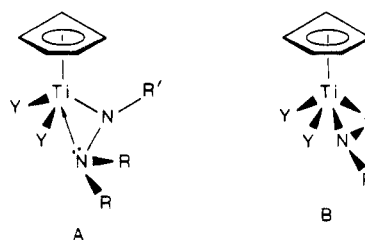
In the hydrazonato(1-) ligand the N(1)N(2)C(2)C(3)C(9) moiety is planar with the Ti(1) atom practically coplanar. The C(1) atom deviates by 0.21 (1) Å from this plane, probably because of the strong steric hindrance between the methyl and phenyl groups. The two phenyl rings are almost perpendicular to each other, the dihedral angle between the two mean planes being 87.7(3)°, thus explaining the $^{13}C\{^1H\}$ NMR results. The N(1)–N(2) bond distance of 1.326 (10) Å is intermediate between the average values for single and double N(sp²)–N(sp²) bonds (1.41 and 1.24 Å, respectively[9]), and the N(2)–C(2) separation of 1.298 (10) Å is slightly longer than the theoretical one, 1.27 Å, for a N(sp²)–C(sp²) double bond and is within the range found in free diazoalkanes (1.28–1.32 Å).[10] These values are also comparable to those found in three hydrazonato(1-) zirconium complexes, where this ligand is bound to the metal in the η^2-fashion [the N–N bonds being 1.338 (4), 1.30 (2) and 1.30 (2) Å and the N–C bonds 1.307 (4), 1.31 (2), and 1.32 (2) Å].[6b] The values for these distances suggest an electronic delocalization over the C–N–N unit and point to the description of the Ph_2CNNMe^- ligand of 3 as a resonance hybrid of the forms depicted in I and II, with an important contribution of form II. This is supported by the IR data discussed above.
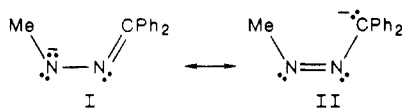
The N(1)–N(2) line is rather perpendicular to the CE–Ti(1) axis [82.2 (3)°] as shown in Figure 2, and precisely this orientation of the hydrazonato ligand determines the location of its phenyl rings pointing toward the Ti(2) fragment.

Bonding Considerations. Leigh et al. have described and characterized by X-ray structures a series of monocyclopentadienyl titanium(IV) hydrazido(1-)[11] and diaz-

enido(1-)[12] complexes and have elaborated a qualitative bonding scheme based on the known molecular orbital diagram of the CpML₂ fragment.[13] The hydrazido(1-) complexes exhibit structure A sketched in Chart I in which the N–N bond and the centroid–Ti axis are coplanar and the TiN₂ plane is a molecular mirror plane, while in the diazenido(1-) complexes B the N–N line is nearly perpendicular to the centroid–Ti axis because in this situation the N–N p orbitals can interact with the Ti d_π orbitals.

The hydrazonato(1-) ligand is isoelectronic with the hydrazido(1-), and consequently a similar structural disposition between them would have been expected. However, the situation of the Ph_2CNNMe^- ligand found in 3, as discussed above, is akin to that of the diazenido(1-) complexes. This behavior indicates that, according to the aforementioned bonding scheme, the Ph_2CNNMe^- ligand uses its delocalized electronic system for charge donation to the electronically deficient metal center, whereas if it were positioned as in A, the Ti orbitals would remain unused.

Chart I

All manipulations were carried out under dry N₂ atmosphere by using Schlenk techniques. Solvents were distilled from drying agents as described elsewhere.[14] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian FT80A and Bruker AC300 instruments. C, H, N analysis were done with a Perkin-Elmer 240B microanalizer. Ph_2CN_2 was prepared as by published procedures.[15]

[TiCp*Me(η^2-MeNNCPh₂)][TiCp*Me₂](μ-O) (3). To a solution of 0.442 g (1 mmol) of (TiCp*Me₂)₂(μ-O) in 15 mL of hexane at -45 °C was added 0.194 g (1 mmol) of Ph_2CN_2 dissolved in 5 mL of hexane dropwise; stirring was continued for 20 min, and the microcrystalline yellow precipitate was filtered, washed with cold hexane, and vacuum dried: yield 78–80%; ^1H NMR (ppm in C₆D₆) 7.85–7.73 (m, 4 H, Ph), 7.30–7.03 (m, Ph), 2.83 (s, 3 H, NMe), 2.04 (s, 15 H, Cp*), 1.89 (s, 15 H, Cp*), 0.79 (s, 3 H, TiMe), 0.76 (s, 3 H, TiMe), 0.60 (s, 3 H, TiMe); ^1H NMR (ppm in THF-d_8) 7.65–7.12 (m, 10 H, Ph), 2.79 (s, 3 H, NMe), 1.98 (s, 15 H, Cp*), 1.81 (s, 15 H, Cp*), 0.42 (s, 3 H, TiMe), 0.30 (s, 3 H, TiMe), 0.09 (s, 3 H, TiMe); $^{13}C\{^1H\}$ NMR (ppm in THF-d_8) 140.86, 137.97, 131.80, 129.05, 128.80, 128.43, 127.83, and 127.52 (Ph), 121.36 (C_5Me_5), 50.70 (NMe), 48.35 (TiMe), 44.97 (TiMe), 40.64 (TiMe), 12.06 (C_5Me_5), 11.85 (C_5Me_5); IR (cm⁻¹, Nujol mull): ν(CN) 1530, ν(TiOTi) 765. Anal. Calcd for $C_{37}H_{52}N_2OTi_2$: C, 69.81; H, 8.23; N, 4.40. Found: C, 69.47; H, 7.84; N, 4.49.

[TiCp*Me(MeNNCPh₂)]₂(μ-O) (4). It was prepared as above from 0.442 g (1 mmol) of (TiCp*Me₂)₂(μ-O) and 0.388 g (2 mmol) of Ph_2CN_2 with an ice-cooled bath: yield 90–92%; ^1H NMR (ppm in C₆D₆) 7.90–7.72 (m, 8 H, Ph), 7.37–6.94 (m, Ph), 2.65 (s, 6 H, NMe), 1.96 (s, 30 H, Cp*), 1.01 (s, 6 H, TiMe); ^1H NMR (ppm in THF-d_8) 7.52–6.96 (m, 20 H, Ph), 2.48 (s, 6 H, NMe), 1.84 (s,

(8) Gómez Sal, M. P.; Mena, M.; Royo, R.; Serrano, R. *J. Organomet. Chem.* **1988**, *358*, 147.

(9) Allman, R. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1975; p 28.

(10) Sorriso, S. In *The Chemistry of the Diazonium and Diazo Groups*, Part 1; Patai, S., Ed.; Wiley: New York, 1978; p 106.

(11) (a) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 385. (b) Hemmer, R.; Thewalt, U.; Hughes, D. L.; Leigh, G. J.; Walker, D. J. *J. Organomet. Chem.* **1987**, *323*, C29.

(12) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 377.

(13) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(14) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1988**, *7*, 258.

(15) Staudinger, H.; Anthes, E.; Pfeninger, F. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 1928.

Table II. Experimental Data for the X-ray Diffraction Study on 3

molecular formula	$C_{37}H_{52}N_2OTi_2$
molecular weight	636.63
cryst system	monoclinic
space group	$P2_1/n$
a, Å	19.372 (4)
b, Å	20.155 (8)
c, Å	9.081 (2)
β, deg	95.13 (2)
V, Å^3	3531 (2)
Z	4
D_{calcd}, g cm^{-3}	1.197
$F(000)$	1360
cryst dimens, mm	0.20 × 0.25 × 0.35
linear absorptn, cm^{-1}	40.75
diffractometer	Siemens AED
scan type	$\theta/2\theta$
scan speed, deg/min	2.5–12
scan width	$(\theta - 0.6) - (\theta + 0.6 + 0.142 \tan \theta)$
radiatn	Ni-filtered Cu Kα ($\bar{\lambda}$ = 1.541 838 Å)
2θ range	6–130
reflctns measd	$\pm h,k,l$
std reflctn	one measd after 50 reflctns
unique total data	6302
unique observed data [$I > 2\sigma(I)$]	2319
R	0.0565
R_w	0.0887

30 H, Cp*), 0.62 (s, 6 H, TiMe); ^{13}C{^{1}H} NMR (ppm in THF-d_8) 142.23, 139.37, 134.96, 133.53, 131.47, 131.40, 130.22, 129.85, 129.74, 128.97, 127.92, and 127.83 (Ph), 121.44 (C_5Me_5), 45.20 (NMe), 41.66 (TiMe), 13.39 (C_5Me_5); IR (cm^{-1}, Nujol mull) ν(CN) 1515, ν(TiOTi) 725. Anal. Calcd for $C_{50}H_{62}N_4OTi_2$: C, 72.28; H, 7.52; N, 6.74. Found: C, 71.94; H, 7.71; N, 6.65.

[TiCp*(MeNNCPh$_2$)][TiCp*Me]$_2$(μ-O)$_3$ (5). A solution of 0.642 g (1 mmol) of [TiCp*Me(μ-O)]$_3$ and 0.6 g (3 mmol) of Ph$_2$CN$_2$ in 50 mL of heptane was heated at reflux overnight. After being cooled to room temperature, the solution was concentrated and cooled to –30 °C and yellow 5 was isolated by filtration. A further crop can be obtained from the mother liquors. The combined yield was 88–90%: ^{1}H NMR (ppm in C$_6$D$_6$) 7.98–7.31 (m, Ph), 2.89 (s, 3 H, NMe), 2.10 (s, 15 H, Cp*), 2.00 (s, 30 H, Cp*), 0.69 (s, 3 H, TiMe), 0.40 (s, 3 H, TiMe); ^{1}H NMR (ppm in THF-d_8) 7.45, 7.36, 7.21 (m, 10 H, Ph), 2.87 (s, 3 H, NMe), 1.96 (s, 15 H, Cp*), 1.92 (s, 15 H, Cp*), 1.89 (s, 15 H, Cp*), 0.30 (s, 3 H, TiMe), 0.05 (s, 3 H, TiMe); ^{13}C{^{1}H} NMR (ppm in THF-d_8) 131.9, 129.9, 129.8, 128.7, 128.5, 128.3, 128.0, 127.2, 127.1, 127.0, 126.6, and 123.4 (Ph), 120.5 (C_5Me_5), 43.6 (NMe), 38.8 (TiMe), 37.2 (TiMe), 12.1 (C_5Me_5), 11.7 (C_5Me_5), and 11.5 (C_5Me_5); IR (cm^{-1}, Nujol mull) ν(CN) 1533, ν(TiOTi) 780. Anal. Calcd for $C_{46}H_{64}N_2O_3Ti_3$: C, 66.03; H, 7.71; N, 3.35. Found: C, 66.10; H, 7.72; N, 3.30.

X-ray Data Collection, Structure Determination, and Refinement for 3. Single crystals of 3 were grown from a toluene–THF mixture at –30 °C and sealed in Lindemann glass capillaries under dry argon, one of which was used for data collection. The crystallographic data are summarized in Table II. Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having 23 < θ < 37°. Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[16] The structure amplitudes were obtained after usual Lorentz and polarization reduction.[17] A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.148 and 0.892, respectively).[18] Only the observed reflections were used

Table III. Fractional Atomic Coordinates (×10^4) for Non-Hydrogen Atoms in 3 with Esd's in Parentheses

atom	x	y	z
Ti(1)	2863 (1)	3272 (1)	545 (2)
Ti(2)	1636 (1)	1926 (1)	465 (2)
O	2188 (3)	2633 (2)	773 (6)
N(1)	2542 (3)	4010 (3)	-725 (8)
N(2)	2192 (3)	4104 (3)	447 (7)
C(1)	2446 (5)	4377 (4)	-2092 (11)
C(2)	1736 (4)	4540 (4)	767 (9)
C(3)	1507 (4)	5113 (4)	-184 (9)
C(4)	1925 (5)	5658 (4)	-376 (11)
C(5)	1697 (6)	6179 (4)	-1277 (12)
C(6)	1046 (6)	6167 (4)	-1977 (12)
C(7)	621 (5)	5649 (4)	-1779 (11)
C(8)	835 (4)	5114 (4)	-867 (10)
C(9)	1422 (4)	4457 (4)	2197 (9)
C(10)	1217 (4)	5026 (4)	2952 (11)
C(11)	941 (5)	4943 (6)	4298 (12)
C(12)	867 (5)	4338 (6)	4905 (12)
C(13)	1055 (5)	3780 (5)	4173 (11)
C(14)	1336 (4)	3843 (4)	2825 (10)
C(15)	3201 (5)	2860 (4)	-1442 (10)
C(16)	3355 (5)	3177 (5)	3010 (11)
C(17)	3740 (5)	2761 (5)	2197 (13)
C(18)	4085 (5)	3172 (8)	1194 (12)
C(19)	3884 (6)	3843 (7)	1500 (15)
C(20)	3440 (5)	3811 (6)	2616 (13)
C(21)	2934 (8)	2942 (8)	4256 (15)
C(22)	3803 (8)	2021 (6)	2323 (19)
C(23)	4629 (6)	2930 (11)	248 (17)
C(24)	4119 (10)	4435 (9)	746 (24)
C(25)	3172 (8)	4411 (7)	3406 (19)
C(26)	2328 (5)	1164 (5)	63 (13)
C(27)	1437 (6)	1675 (6)	2639 (12)
C(28)	806 (4)	2477 (4)	-1136 (10)
C(29)	437 (4)	2176 (4)	-89 (11)
C(30)	484 (4)	1491 (5)	-303 (13)
C(31)	890 (6)	1360 (6)	-1419 (14)
C(32)	1098 (5)	1989 (6)	-1938 (11)
C(33)	862 (7)	3220 (5)	-1406 (15)
C(34)	11 (7)	2531 (8)	992 (15)
C(35)	92 (7)	983 (7)	571 (19)
C(36)	1029 (9)	698 (7)	-2099 (22)
C(37)	1534 (7)	2102 (10)	-3226 (14)

in the structure solution and refinement.

The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms of the methyl groups at C(1), C(15), C(26), and C(27) were localized in the final difference Fourier map, but not refined; all the remaining ones were placed at their geometrically calculated positions and introduced in the final structure factor calculation. The final cycles of refinement were carried out on the basis of 382 variables; after the last cycle, no parameters shifted by more than 0.5 esd. The biggest remaining peak in the final difference map was equivalent to about 0.27 e/Å^3; in the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the K and g values were 0.5285 and 0.0198, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 19. The final atomic coordinates for the non-hydrogen atoms are given in Table III. The atomic coordinates of the hydrogen atoms are given in Table SII and thermal parameters in Table SIII.

(16) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

(17) Data reduction, structure solution, and refinement were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio, Bologna) and on the GOULD-SEL 32/77 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 system of crystallographic computer programs (Sheldrick, G. M. *Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976).

(18) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1983**, *A39*, 158. The program ABSORB was used (Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109).

(19) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Crystal Structures of the Clusters [Os₃H₂($\overline{\text{XCH}=\text{CHC}=\text{C}}$)(CO)₉] Where X = NMe or S Containing Triply Bridging Ligands Derived from *N*-Methylpyrrole and Thiophene

Antony J. Deeming*

Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, Great Britain

Alejandro J. Arce and Ysaura De Sanctis

Chemistry Center, Instituto Venezolano Investigaciones Cientificas, Apartado 21827, Caracas 1020-A, Venezuela

Michael W. Day and Kenneth I. Hardcastle

Department of Chemistry, California State University, Northridge, 18111 Nordhoff Street, Northridge, California 91330

Received August 8, 1988

The single-crystal X-ray structures are reported of two complexes containing ligands derived from *N*-methylpyrrole and thiophene respectively: [Os₃H₂($\overline{\text{XCH}=\text{CHC}=\text{C}}$)(CO)₉] (1, X = NMe; 2, X = S). Both complexes are structurally related with σ-Os-C bonds at the 2- and 3-positions of the rings and with an η^2-coordination to the third metal atom. Crystals of 1 are triclinic, $P\bar{1}$, with a = 14.762 (2) Å, b = 15.765 (4) Å, c = 8.949 (1) Å, α = 94.60 (2)°, β = 99.37 (1)°, γ = 70.74 (2)°, Z = 4, and R_w = 0.050 for 3451 reflections, while those of 2 are monoclinic, $P2_1/c$, with a = 16.315 (2) Å, b = 13.091 (2) Å, c = 17.347 (2) Å, β = 92.05 (1)°, Z = 8, and R_w = 0.050 for 2256 reflections. Compound 2 contains two independent molecules in the unit cell, one of which is best modeled by the C₄H₂S ligand disordered in two possible orientations, each 50% populated. Compound 1, likewise, has two independent molecules in the unit cell but without disorder. These structures are compared with that of the benzyne complex [Os₃H₂(μ_3,η^2-C₆H₄)(CO)₉] (3) which adopts a parallel geometry and with the (diethylamino)ethyne analogue [Os₃H₂(Et₂NC₂H)(CO)₉] (4) in which the ligand is perpendicular to an Os-Os edge. The geometry of 1, and to a lesser extent that in 2, is distorted from the parallel toward the perpendicular type, and the effect of the heteroatom in the organic ring on this distortion is discussed.

Introduction

Furan,[1] thiophene,[2] and pyrrole[2,3] ligands may be introduced into triosmium clusters in dehydrogenated forms as triply bridging ligands. The cluster [Os₃(CO)₁₂] reacts directly with *N*-methylpyrrole (C₄H₄NMe) to give the cluster [Os₃H₂(C₄H₂NMe)(CO)₉] (1) in which the dehydrogenated ligand (C₄H₂NMe) behaves as a four-electron donor[3] and which relates to known alkyne[4-6] or aryne[4,7,8] clusters. A more satisfactory route to such species is from the 2-formyl-substituted derivatives which add oxidatively to [Os₃(CO)₁₀(MeCN)₂] to give acyl clusters.[2] For example,

Scheme I

(1) (X = NMe)
(2) (X = S)
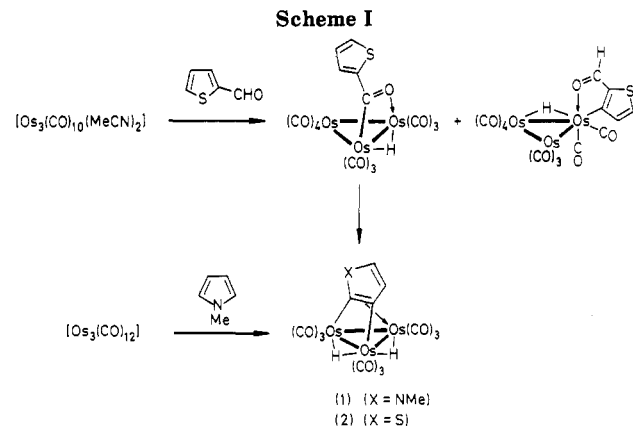
2-formylthiophene reacts in this way at the formyl function to give [Os₃H($\overline{\text{SCH}=\text{CHCH}=\text{CCO}}$)(CO)₁₀] but also metalates at a ring site to give an isomer, [Os₃H($\overline{\text{SC-}}$ $\overline{\text{H}=\text{CHC}=\text{CCHO}}$)(CO)₁₀] (Scheme I). The acyl isomer doubly decarbonylates in refluxing cyclohexane to give a compound that is a subject of this paper, the dihydride

(1) Himmelreich, D.; Muller, G. *J. Organomet. Chem.* **1985**, *297*, 341.
(2) Acre, A. J.; De Sanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1986**, *311*, 371.
(3) Choo Yin, C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 2563.
(4) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415.
(5) Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Organomet. Chem.* **1975**, *97*, C16.
(6) Deeming, A. J. *J. Organomet. Chem.* **1978**, *150*, 123.
(7) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2257.
(8) Gallop, M. A.; Johnson, B. F. G.; Lewis, J.; McCamley, A.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1988**, 1071.