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Synthesis of dinuclear iron and ruthenium aminoalkylidene complexes and the molecular structure of the novel *cis*-$[Ru_2(CO)_2(Cp)_2\{\mu\text{-}C(CN)N(Me)Bz\}_2]$ ($Cp = \eta\text{-}C_5H_5$; $Bz = CH_2Ph$) ☆

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Abstract

Repeated stepwise addition of $CH_3SO_3CF_3$ and Bu_4NCN to the diisocyanide complex $[Ru_2(CO)_2(Cp)_2(CNBz)_2]$ ($Cp = \eta\text{-}C_5H_5$; $Bz = CH_2Ph$) has led to the formation of the new bis-μ-aminoalkylidene complex $[Ru_2(CO)_2(Cp)_2\{\mu\text{-}C(CN)N(Me)Bz\}_2]$, which has been characterized by X-ray diffraction. The crystal contains a racemic mixture of the isomer with the same chirality at the amine nitrogens. The molecule conforms to a C_2 idealized symmetry. Selected bond distances are Ru—Ru 2.662(1), Ru—(μ-C) 2.088 (av), μ-C—N(amine) 1.479 (av) Å. All the intermediate species: $[Ru_2(CO)_2(Cp)_2(\mu\text{-}CNBz)\{\mu\text{-}CN(Me)Bz\}SO_3CF_3$, $[Ru_2(CO)_2(Cp)_2(\mu\text{-}CNBz)\{\mu\text{-}C(CN)N(Me)Bz\}]$ and $[Ru_2(CO)_2(Cp)_2\{\mu\text{-}CN(Me)Bz\}\{\mu\text{-}C(CN)N(Me)Bz\}]SO_3CF_3$ have been isolated and characterized spectroscopically. Attempts to extend the synthetic method to the iron diisocyanide $[Fe_2(CO)_2(Cp)_2(CNBz)_2]$ led to $[Fe_2(CO)(CNBz)(Cp)_2(\mu\text{-}CO)\{\mu\text{-}CN(Me)Bz\}]SO_3CF_3$ and $[Fe_2(CO)(CNBz)(Cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)N(Me)Bz\}]$ but not to the bis(aminoalkylidene) derivative.

Keywords: Iron; Ruthenium; Aminoalkylidene; X-ray diffraction; Alkylidyne; Isocyanide

1. Introduction

We have recently described two different synthetic methods for obtaining dinuclear μ-aminoalkylidene complexes, which still remain a poorly explored class of compounds [1] compared with the vast literature on μ-alkylidene complexes. The first method [2] requires the displacement of SMe_2 from the sulfonium complex $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe_2)(CN)\}]SO_3CF_3$ [3] by secondary amines (HNR_2) to give the complexes $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CO)\{\mu\text{-}C(NR_2)(CN)\}]$. The second consists in a stepwise N-alkylation ($R'SO_3CF_3$) and CN^- addition of the isocyanide complexes $[M_2(CO)_3(Cp)_2(CNR)]$ (M = Fe, R = CH_2Ph or C(O)SMe; M = Ru, R = CH_2Ph). This leads to the formation of the corresponding μ-cyanoaminoalkylidene derivatives $[M_2(CO)_2(Cp)_2(\mu\text{-}CO)\{\mu\text{-}C(NRR')(CN)\}]$ [4,5].

Here we report an extension of the second method to the diisocyanide complexes $[M_2(CO)_2(Cp)_2(CNBz)_2]$ (M = Ru or Fe; Bz = CH_2Ph) with the aim of obtaining bis(μ-aminoalkylidene) complexes.

2. Results and discussion

Dinuclear complexes bridged by CNR ligands are known to be susceptible to protonation or alkylation at the nitrogen atom. [6]. Recently reported re-investigations [6e] on the alkylation of the complexes $[Fe_2(Cp)_2(CO)_2(CNR)_2]$ have shown that one or both of the isocyanides can be alkylated, depending on the amount of $R'SO_3CF_3$ used. We have now found that the ruthenium diisocyanide complex $[Ru_2(CO)_2$-

☆ Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday.

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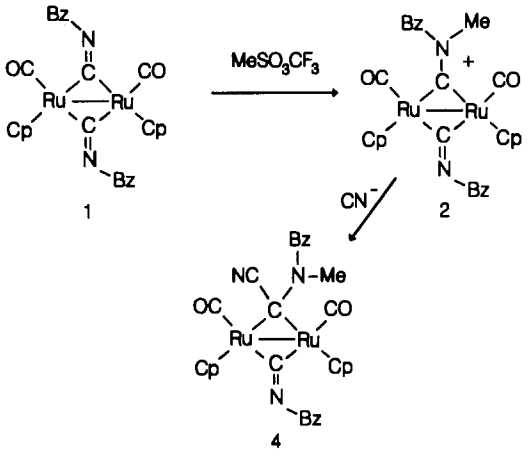


Scheme 1.

$(Cp)_2(\mu\text{-CNBz})_2]$ (**1**), readily obtained by Me_3NO-induced CO substitution of $[Ru_2(CO)_4(Cp)_2]$ [5], reacts with an equimolar amount or a large excess of $MeSO_3CF_3$ to form the complexes $[Ru_2(CO)_2(Cp)_2(\mu\text{-CNBz})\{\mu\text{-CN(Me)Bz}\}]SO_3CF_3$ (**2**) (Scheme 1) or $[Ru_2(CO)_2(Cp)_2\{\mu\text{-CN(Me)Bz}\}_2](SO_3CF_3)_2$ (**3**), respectively.

The spectroscopic properties of complex **2** indicate bridging by the CN(Me)Bz: δ_C at 298.6 ppm attributable to the μ-C and ν(C=N) absorptions at 1594 and 1581 cm^{-1}. It is not obvious why two absorptions are observed for the μ-CNRR′ instead of the one expected at ca. 1600 cm^{-1} (e.g. for $[Ru_2(CO)_2(Cp)_2(\mu\text{-CO})\{\mu\text{-CN(Me)Bz}\}]^+$ at 1595 cm^{-1}) [5]. However, in cases such as $[Fe_2(CO)_2(Cp)_2(\mu\text{-CO})(\mu\text{-CNMeR})]I$ (R = allyl or Bz), a multiplet absorption band attributed to ν(C=N) was observed [6c]. The IR spectrum exhibits ν(CO) bands at 2016 (s), 1985 (w) and 1823 (m) cm^{-1}, suggesting that complex **2** adopts a *cis* geometry (with both CO on the same side of the Ru—Ru vector), as usually observed in the analogous Fe and Ru cationic complexes [5,6e], and a ν(C=N) absorption at 1756 cm^{-1}, attributable to μ-CNBz. Moreover, one IR ν(CN) absorption at 2168 cm^{-1} indicates the presence of an isomeric form bearing terminally coordinated CNBz. Comparison with the analogous diiron complexes $[Fe_2(CNR)(CO)(Cp)_2(\mu\text{-CO})(\mu\text{-CNRR'})]^+$ (R and R′ = alkyl) in which the CNR are exclusively terminally coordinated [6e], shows the tendency of isocyanide towards bridging in diruthenium complexes. The inequivalence of the Cp (δ 91.9 and 91.8 ppm) and CO (δ 198.0 and 197.3 ppm) observed in the ^{13}C NMR spectrum of **2** indicates hindered rotation around the μ-C=N bond, as found in the related $[Ru_2(CO)_2(Cp)_2(\mu\text{-CO})(\mu\text{-CN(Me)Bz})]^+$ [5].

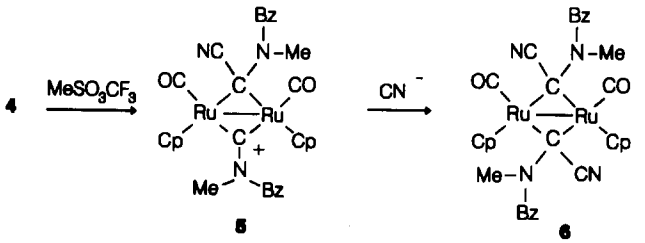
The reactivity of the μ-CNRR′ moieties, which are commonly viewed as aminocarbyne or iminium ligands [6,7], is almost unexplored [6g]. Exceptions are the additions of nucleophiles (CN^- or H^-) in diiron and diruthenium cationic complexes [4,5] to the bridging carbon which has electrophilic character. We have found that complex **2** reacts with $(Bu_4N)CN$ to give the μ-aminocyanoalkylidene complex $[Ru_2(CO)_2(Cp)_2(\mu\text{-CNBz})\{\mu\text{-C(CN)N(Me)Bz}\}]$ (**4**) (Scheme 1).

The spectroscopic properties of **4** are similar to those reported for the closely related complex $[Ru_2(CO)_2(Cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)N(Me)Bz}\}]$ [5]. Two IR ν(CN) absorptions, attributable to the C≡N and μ-CNBz groups, are observed at 2151 and 1717 cm^{-1}, respectively. The two ν(CO) bands at 1998 (s) and 1964 (w) cm^{-1} indicate the presence of two *cis* terminally bonded CO groups. These observations are consistent with the single Cp resonance in both the ^1H (δ 5.26 ppm) and ^{13}C (δ 92.5 ppm) NMR spectra and with the observed ^{13}C resonances at δ 223.4 and 198.2 ppm attributable to the μ-*C*NBz and CO carbons, respectively. The μ-alkylidyne to μ-alkylidene carbon conversion is accompanied by a significant high field shift in the ^{13}C NMR resonance of the bridging carbon, from δ 298.6 ppm to δ 139.4 ppm. The spectroscopic data for **4** clearly indicate the existence of a single *cis* isomer in solution, bearing the CNR and cyano-aminoalkylidene [C(CN)NRR′] in bridging positions. Comparison with the analogous diiron complexes $[Fe_2(CO)_2(Cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)NRR'}\}]$, in which the cyano-aminoalkylidene ligands may adopt either bridging or terminal coordination [2], shows that, like the CNR, the aminoalkylidene exhibits a higher tendency to bridging in the diruthenium complexes.

Complex **4** undergoes the sequence of reactions described in Scheme 1 in order to convert the remaining CNBz into a second μ-cyanoaminoalkylidene ligand. Indeed, it is readily alkylated at the nitrogen atom of the isocyanide, affording $[Ru_2(CO)_2(Cp)_2\{\mu\text{-CN(Me)Bz}\}\{\mu\text{-C(CN)N(Me)Bz}\}]SO_3CF_3$ (**5**) isolated as a yellow microcrystalline solid (Scheme 2).

As in complex **2**, the μ-CN(Me)Bz in **5** gives rise to two ν(CN) absorptions at 1597 and 1581 cm^{-1}, whereas the usual ν(CO) bands pattern [2029 (s) and 1996 (w) cm^{-1}] is shown in the IR spectrum. The addition of $(NBu_4)CN$ to a dichloromethane solution of **5** yields the bis(μ-aminoalkylidene) complex $[Ru_2(CO)_2(Cp)_2\{\mu\text{-C(CN)N(Me)Bz}\}_2]$ (**6**) (Scheme 2).

A few bis(μ-alkylidene) diruthenium complexes are



Scheme 2.

known [8], but to our knowledge compound **6** is the first bis(μ-aminoalkylidene) complex. For this reason we have studied the solid-state structure of **6** by X-ray diffraction. The molecular geometry is illustrated in Fig. 1. It consists of two Ru(CO)(Cp) groups bound together in a *cis* configuration and two alkylidenes C(CN)N(Me)Bz symmetrically bridging the Ru—Ru bond. The bridging ligands are oriented orthogonally to the Ru—Ru axis with the more hindering amine groups N(Me)Bz facing the CO ligand and the Me and Bz terminations pointing away from these ligands. The μ-C—Ru_2 planes are tilted away from the Cp (dihedral angle 23°). All these molecular features can be explained in terms of optimization of the intramolecular contacts. The overall molecular symmetry would be C_{2v} if the phenyl rings were ignored, but the actual symmetry is C_2 because the amine nitrogens, N(1) and N(2), are chiral centres with the same chirality. The crystal, however, contains the racemic mixture.

The spectroscopic properties of **6** are consistent with the molecular structure. Two IR ν(CO) absorptions (at 2010 (s) and 1981 (w) cm^{-1}) and one single Cp resonance in both the ^1H (δ 5.34 ppm) and ^{13}C (δ 96.4 ppm) NMR spectra are observed, indicating the existence, in solution of only one *cis* isomer, which is presumably the one bearing the CN group on the less hindered Cp side of the molecule. Assignment of the

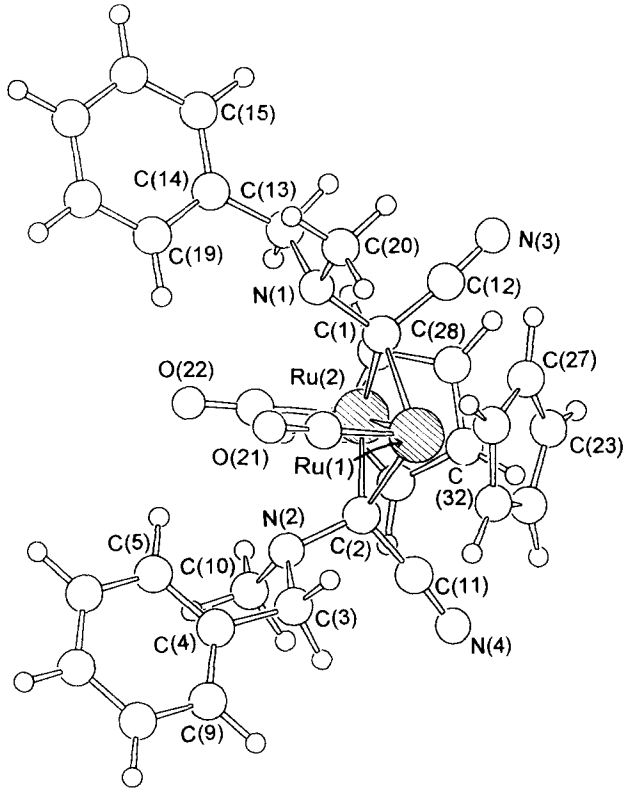


Fig. 1. Molecular configuration of *cis*-[$Ru_2(CO)_2(Cp)_2$\{μ-C(CN)N(Me)Bz\}$_2$] (**6**) of idealized C_2 symmetry.

Table 1
Selected bond lengths (Å) and angles (°) for [$Ru_2(CO)_2(Cp)_2$\{μ-C(CN)N(Me)Bz\}$_2$] (**6**)

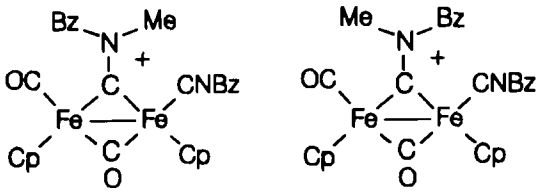
Ru(1)—Ru(2)	2.662(1)	C(2)—N(2)	1.473(7)
Ru(1)—C(1)	2.087(6)	C(2)—C(11)	1.446(9)
Ru(2)—C(1)	2.075(6)	C(11)—N(4)	1.16(1)
Ru(1)—C(2)	2.079(6)	N(2)—C(10)	1.471(8)
Ru(2)—C(2)	2.104(6)	N(2)—C(3)	1.489(7)
C(1)—N(1)	1.485(7)	C(3)—C(4)	1.502(7)
C(1)—C(12)	1.460(9)	Ru(1)—C(21)	1.846(6)
C(12)—N(3)	1.16(1)	C(21)—O(21)	1.124(8)
N(1)—C(13)	1.500(7)	Ru(2)—C(22)	1.858(7)
N(1)—C(20)	1.463(7)	C(22)—O(22)	1.141(8)
C(13)—C(14)	1.491(7)	Ru(1)—C(Cp) (av.)	2.285(8)
Ru(2)—C(Cp) (av.)	2.260(6)		
Ru(1)—C(1)—Ru(2)	79.5(2)	N(2)—C(2)—C(11)	108.9(5)
Ru(1)—C(2)—Ru(2)	79.1(2)	C(2)—N(2)—C(10)	112.3(5)
N(1)—C(1)—C(12)	107.8(5)	C(2)—N(2)—C(3)	112.4(5)
C(1)—N(1)—C(13)	112.2(5)	C(3)—N(2)—C(10)	109.1(5)
C(13)—N(1)—C(20)	109.1(5)	N(2)—C(3)—C(4)	112.9(5)
C(1)—N(1)—C(20)	111.1(5)	C(2)—C(11)—N(4)	177.4(8)
N(1)—C(13)—C(14)	112.1(5)	Ru(1)—C(21)—O(21)	174.8(6)
C(1)—C(12)—N(3)	174.9(7)	Ru(2)—C(22)—O(22)	175.9(5)
Ru(1)—C(1)—N(1)	118.6(4)	Ru(1)—C(2)—N(2)	121.6(4)
Ru(2)—C(1)—N(1)	120.9(4)	Ru(2)—C(2)—N(2)	118.6(4)
Ru(1)—C(1)—C(12)	114.2(4)	Ru(2)—C(1)—C(12)	113.8(4)
Ru(1)—C(2)—C(11)	114.0(5)	Ru(2)—C(2)—C(11)	111.9(4)

^{13}C NMR resonances to the CN, the μ-alkylidene and the aromatic carbon atoms in **6** has been done by comparison with the corresponding values reported for the complex [$Ru_2(CO)_2(Cp)_2$(μ-CO)\{μ-C(CN)N(Me)Bz\}] in which correct attribution was obtained by ^{13}C isotope enrichment [5]. The NMR data, exhibiting one single resonance for the Me (δ_H at 2.53 ppm, δ_C at 45.5 ppm) as well as for the CH_2Ph (δ_H at 4.09 ppm, δ_C at 65.8 ppm) do not suggest a mixture of diastereisomers in solution arising from the configurations adopted at the N(1) and N(2) chiral centres. In fact our data on a crystal containing the isomer with the same chirality at both the amine nitrogens (Fig. 1) does not exclude the presence of the diastereisomer with N(1) and N(2) of opposite chirality. Moreover, interconversion of diastereoisomers in solution may arise from inversion at the N atoms and rotation around the μ-C—N amine bonds. These processes are not detectable at room temperature on the NMR time scale.

The Ru—Ru separation, 2.662(1)Å (see Table 1), is shorter than that found in the parent monoalkylidene derivative [$Ru_2(CO)_2(Cp)_2$(μ-CO)\{μ-C(CN)N(Me)Bz\}], i.e. 2.711(1)Å [5]. If the Ru—Ru distance in the carbonyl [$Ru_2(CO)_2(Cp)_2$(μ-CO)$_2$] (2.735(2)Å) [9] is also considered, a trend is evident and the ability of the bridging alkylidene in reinforcing the M—M bond is confirmed. The bridging μ-C(CN)N(Me)Bz are equivalent to each other and to the geometry found in the monofunctionalized [$Ru_2(CO)_2(Cp)_2$(μ-CO)\{μ-C(CN)N(Me)Bz\}]. The angle at the carbene carbon C(CN)—

(μ-C)—N(amine), average 108.3°, is as usual lower than expected for an sp^2 carbon. We have already explained this feature as an effect of steric pressure of the carbene pπ orbital on the μ-C—C(CN) and μ-C—N(amine) bonds [10]. The Ru—μ-C(alkylidene) mean distance, 2.086 Å, is longer than the average value for Ru—μ-C(carbonyl) (2.03 Å) [5,9]. This difference can be ascribed to the different hybridization of the two kinds of bridging carbons. The other bonds to bridging carbons, μ-C—C(cyanide) and μ-C—N(amine), have mean values of 1.453 and 1.479 Å, respectively, suggesting little involvement of the CN group in the π-bonding centred at the carbene atom.

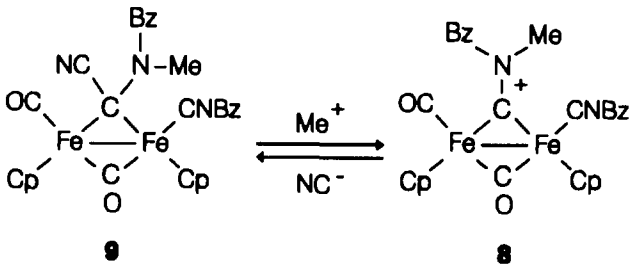
The sequences of reactions described in Schemes 1 and 2 have also been extended to the corresponding diiron complex $[Fe_2(CO)_2(CNBz)_2(cp)_2]$. The compounds $[Fe_2(CO)_2(CNR)_2(Cp)_2]$ are usually prepared by reaction of $[Fe_2(CO)_4(Cp)_2]$ with CNR in refluxing xylenes. However, where R is benzyl, yields are very low and the monosubstituted derivative $[Fe_2(CO)_3(CNBz)(Cp)_2]$ is by far the predominant product [11]. We have found that a more convenient access to the iron counterpart of **2**, $[Fe_2(CO)(CNBz)(Cp)_2(\mu\text{-CO})\{\mu\text{-CN(Me)Bz}\}]SO_3CF_3$ (**8**), consists in reaction of the cationic complex $[Fe_2(CO)_2(Cp)_2(\mu\text{-CO})\{\mu\text{-CN(Me)Bz}\}]SO_3CF_3$ (**7**) [12] with benzyl isocyanide. In fact the μ-aminocarbyne complex **7** undergoes CO substitution more readily than does the parent isocyanide compound $[Fe_2(CO)_3(CNBz)(Cp)_2]$. The CNBz is terminally coordinated in **8** whereas in the ruthenium counterpart **2** it may adopt both bridging and terminal positions. The spectroscopic properties of **8** are consistent with those of the analogous $[Fe_2(CO)(CNR)(Cp)_2(\mu\text{-CO})\{\mu\text{-CNRR'}\}]^+$ (R and R' = Me or Et) complexes [6e] consisting of a mixture of two isomers (α and β forms) in solution.



(α and β forms)

These isomers give rise to two sets of resonances (of about the same intensity) in the ^1H NMR spectrum, although it is not possible to assign them (e.g. for **8** signals at δ 4.76 ppm and δ 4.68 ppm are observed for the CH_2 protons of the $CNCH_2Ph$ ligand; likewise resonances at δ 4.12 ppm and δ 4.08 ppm are attributable to the Me group).

As do compounds **5** and **2**, complex **8** readily undergoes CN^- addition at the μ-C carbon to give the μ-cyanoaminoalkylidene $[Fe_2(CO)(CNBz)(Cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)N(Me)Bz}\}]$ (**9**). The IR spectrum of **9**



Scheme 3.

shows a strong absorption at 2139 cm^{-1} assigned to the ν(CN) of the terminally bonded CNBz, and bands at 1964 and 1778 cm^{-1} due to the terminal and bridging CO, respectively. Moreover, two weak absorptions are observed at 1995 and 1728 cm^{-1}, suggesting the presence of a smaller amount of the isomer in which the CNBz is bridging and both CO are terminal. However, the ^1H NMR spectrum of **9** exhibits only two equally intense resonances for the Cp (at δ 4.76 and 4.62 ppm).

Complex **9** has been treated with $CH_3SO_3CF_3$ in an attempt to methylate the nitrogen atom of the CNBz. In contrast to the analogous reaction of **4**, treatment of **9** with $MeSO_3CF_3$ results in the formation of **8** (Scheme 3), thus reversing the μC cyanide reaction.

Elimination of CN^- from the μ-cyanoaminoalkylidene complexes $[Fe_2(CO)_2(Cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)N(R)R'}\}]$ (R = R' = Me; NRR' = piperidyl) upon treatment with $MeSO_3CF_3$ or with $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) has previously been observed and interpreted on the basis of the high stability of the μ-aminoalkylidyne ligand (CNRR') in the diiron complexes [13]. We therefore conclude that the stepwise methylation and cyanide addition route cannot be applied to the synthesis of bis(aminoalkylidene) complexes in the case of iron.

3. Experimental details

3.1. General

All reactions were carried out routinely under dinitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under dinitrogen from appropriate drying agents. Instruments employed: IR, Perkin-Elmer 983-G; NMR, Varian Gemini 200. Elemental analyses were by Pascher Microanalytical Laboratory (Remagen, Germany). The complexes $[Fe_2(CO)_4(Cp)_2]$ and $[Ru_2(CO)_4(Cp)_2]$ were purchased from Strem and used as received. Compounds $[Ru_2(CO)_2(Cp)_2(\mu\text{-CNBz})_2]$ (**1**) [5] and $[Fe_2(CO)_2(Cp)_2(\mu\text{-CO})\{\mu\text{-CN(Me)Bz}\}]$ (**7**) [12] were prepared according to published methods.

3.2. Synthesis of $[Ru_2(CO)_2(Cp)_2(\mu\text{-}CNBz)\{\mu\text{-}CN(Me)Bz\}]SO_3CF_3$ (2)

A dichloromethane solution (20 cm^3) of **1** (0.24 g, 0.39 mmol) was stirred with a slight excess of $CH_3SO_3CF_3$ (66 mg, 0.40 mmol) for 10 min. The solution was then evaporated to dryness in vacuo and the residue washed with Et_2O and redissolved in CH_2Cl_2. The addition of Et_2O gave a yellow microcrystalline precipitate of complex **2** (0.17 g, 54%). Analysis. Found: C, 45.51; H, 2.75%. $C_{30}H_{27}F_3N_2O_5SRu_2$ requires: C, 45.80; H, 3.46%. IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$ 2016 (s), 1985 (w) (CO); 1823 (m) (μ-CO); 2168 (m) (CN); 1756 (s), 1594 (mw), 1581 (w) (C=N). NMR: δ_H ($CDCl_3$): 7.40–7.27 (10H, m, Ph); 5.70 (10H, s, br, Cp); 5.63 (m, μ-CN(Me)CH_2Ph); 4.86 (2H, s, μ-CNCH_2Ph); 3.81 (3H, s, Me) ppm. δ_C ($CDCl_3$): 298.6 (μ-*C*N(Me)Bz); 198.0, 197.3 (CO); 138.1, 133.7, 130.2, 129.8, 129.7, 128.7 128.4, 127.7 (Ph); 91.9, 91.8 (Cp); 71.9, 64.9 (N*C*H_2Ph); 51.4 (NMe) ppm.

3.3. Synthesis of $[Ru_2(CO)_2(Cp)_2\{\mu\text{-}CN(Me)Bz\}_2]SO_3CF_3)_2$ (3)

Complex **1** (0.40 g, 0.64 mmol) was allowed to react with a large excess of $MeSO_3CF_3$ (0.43 g, 2.64 mmol) in CH_2Cl_2 (20 cm^3) for 24 h. The solution was then evaporated to dryness in vacuo and the residue washed with Et_2O and redissolved in CH_2Cl_2. Addition of Et_2O gave a yellow microcrystalline precipitate of complex **3** (0.32 g, 53%). Samples of **3** were contaminated with variable amounts (less than 10%) of compound **2**. IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$: 2044 (s), 2018 (w) (CO); 1611 (m) (C=N). NMR: δ_H (CD_2Cl_2): 7.50–7.29 (10H, m, Ph); 6.23 (10H, s, Cp); 5.85 (2H, d, $J_{AB} = 14$ Hz, μ-CNCH_2Ph); 5.40 (2H, d, $J_{AB} = 14$ Hz, μ-CNCH_2Ph); 3.90 (3H, s, Me) ppm.

3.4. Synthesis of $[Ru_2(CO)_2(Cp)_2(\mu\text{-}CNBz)\{\mu\text{-}C(CN)N(Me)Bz\}]$ (4)

To a stirred solution of **2** (0.43 g, 0.55 mmol) in CH_2Cl_2 (30 cm^3) was added $(NBu_4)CN$ (0.15 g, 0.55 mmol). After 15 min the mixture was filtered through an alumina pad. The yellow solution was evaporated to dryness under reduced pressure and the residue crystallized from CH_2Cl_2 layered with pentane at −20°C. Yield, 0.18 g (50%). Analysis: Found; C, 54.60; H, 4.10%. $C_{30}H_{27}N_3O_2Ru_2$ requires: C, 54.29; H, 4.10%. IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$: 1998 (s), 1964 (w) (CO); 2151 (w) (CN); 1717 (m) (C=N). NMR: δ_H (CD_2Cl_2): 7.38–7.20 (10H, m, Ph); 5.26 (10H, s, Cp); 4.78 (2H, s, μ-CNCH_2Ph); 4.10 (s, 2H, N(Me)CH_2Ph); 2.51 (3H, s, Me) ppm. δ_C ($CDCl_3$): 223.4 (μ-*C*NBz); 198.2 (CO); 139.4 (μ-C); 127.7 (CN); 140.1, 139.9, 129.3, 129.1, 128.9, 127.9, 127.4 127.3 (Ph); 92.5 (Cp); 65.6, 64.6 (N*C*H_2Ph); 45.3 (NMe) ppm.

3.5. Synthesis of $[Ru_2(CO)_2(Cp)_2\{\mu\text{-}CN(Me)Bz\}\{\mu\text{-}C(CN)N(Me)Bz\}]SO_3CF_3$ (5)

A dichloromethane solution (20 cm^3) of **4** (0.16 g, 0.24 mmol) was treated with a slight excess of $CH_3SO_3CF_3$ (43 mg, 0.26 mmol). The mixture was stirred for 15 min and then volatile material then removed under vacuum. The residue was washed with Et_2O and redissolved in CH_2Cl_2. Addition of Et_2O gave a yellow-orange microcrystalline precipitate of complex **5** (0.10 g, 53%). Analysis: Found; C, 46.35; H, 3.50%. $C_{32}H_{30}F_3N_3O_5SRu_2$ requires; C, 46.45; H, 3.36%. IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$: 2029 (s), 1996 (w) (CO); 2164 (W) (CN); 1597 (m), 1581 (w) (C=N). NMR: δ_H (CD_2Cl_2): 7.44–7.30 (10H, m, Ph); 5.88 (10H, s, br, Cp); 5.62–5.40 (2H, m, μ-CN(Me)CH_2Ph); 4.28 (2H, s, μ-C(CN)N(Me)CH_2Ph); 3.76 (3H, s, μ-CN(*Me*)Bz); 2.65 (3H, s, μ-C(CN)N(*Me*)Bz) ppm.

3.6. Synthesis of $[Ru_2(CO)_2(Cp)_2\{\mu\text{-}(CN)N(Me)Bz\}_2]$ (6)

To a solution of **5** (0.15 g, 0.18 mmol) in CH_2Cl_2 (20 cm^3) was added $(NBu_4)CN$ (0.06 g, 0.22 mmol). The mixture was stirred for 15 min and then filtered through an alumina pad. Evaporation of the solvent in vacuo and recrystallization of the residue from CH_2Cl_2 layered with pentane at −20°C gave yellow crystals of **6** (75 mg, 59%). Analysis: Found: C, 54.42; H, 4.30%. $C_{32}H_{30}N_4O_2Ru_2$ requires: C, 54.57; H, 4.26% IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$: 2010 (s), 1981 (w) (CO); 2157 (w) (CN). NMR: δ_H ($CDCl_3$): 7.34–7.27 (10H, m, Ph); 5.34 (10 H, s, Cp); 4.09 (4H, s, NCH_2Ph); 2.53 (6H, s, Me) ppm. δ_C ($CDCl_3$): 198.7 (CO); 139.9 (μ-C); 127.7 (CN); 145.7, 129.2, 128.0 (Ph); 96.4 (Cp); 65.8 (*C*H_2Ph); 45.5 (NMe) ppm.

3.7. Synthesis of $[Fe_2(CO)(CNBz)(Cp)_2(\mu\text{-}CO)\{\mu\text{-}CN(Me)Bz\}]SO_3CF_3$ (8)

A mixture of $[Fe_2(CO)_2(Cp)_2(\mu\text{-}CO)\{\mu\text{-}CN(Me)Bz\}]SO_3CF_3$ (7) (1.68 g, 2.77 mmol) and benzylisocyanide (0.73 g, 6.62 mmol) was heated in benzene (30 cm^3) at reflux for 3 h. The volatiles were then removed under reduced pressure and the residue crystallized from a CH_2Cl_2/Et_2O mixture affording red crystals of **8** (1.54 g, 80%). Analysis: Found: C, 51.64; H, 3.98%. $C_{30}H_{27}F_3Fe_2N_2O_5S$ requires: C, 51.74; H, 3.91%. IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$: 1986 (s) (CO); 1820 (ms) (μ-CO); 2158 (m) (CN); 1565 (mw) (C=N). NMR: δ_H ($CDCl_3$):

7.56–7.25 (10H, m, Ph); 6.08–5.65 (2H, m, μ-CN(Me)CH_2Ph); 5.30, 5.26, 5.17 (10H, s, Cp); 4.76, 4.68 (2H, s, CNCH_2Ph); 4.12, 4.08 (3H, s, Me) ppm.

3.8. Synthesis of $[Fe_2(CO)(CNBz)(Cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)N(Me)Bz\}]$ (9)

To a CH_2Cl_2 solution (20 cm^3) of **8** (0.21 g, 0.30 mmol) was added $(NBu_4)CN$ (94 mg, 0.35 mmol). The mixture was stirred for 2 h and filtered through an alumina pad. Evaporation of the solvent under reduced pressure and crystallization from CH_2Cl_2 layered with pentane at −20°C gave red crystals of **9** (0.05 g, 28%). Analysis: Found: C, 63.00; H, 4.77%. $C_{30}H_{27}Fe_2N_3O_2$ requires: C, 62.85; H, 4.75%. IR (CH_2Cl_2) ν_{max}(cm^{-1}): 1995 (mw), 1964 (s) (CO); 1778 (m) (μ-CO); 2139 (s) (CN); 1728 (w) (C=N). NMR: δ_H ($CDCl_3$): 7.34–7.20 (10H, m, Ph); 4.76, 4.62 (10H, s, Cp); 4.38 (1H, d, J_{AB} = 14 Hz); 4.36 (1H, d, J_{AB} = 16 Hz); 4.26 (1H, d, J_{AB} = 16 Hz); 4.23 (1H, d, J_{AB} = 14 Hz) (CH_2Ph); 2.66 (3H, s, Me) ppm.

Table 2
Crystal data and experimental details for $[Ru_2(CO)_2(Cp)_2\{\mu\text{-}C(CN)N(Me)Bz\}_2]$ $0.75CH_2Cl_2$

Formula	$C_{32}H_{30}N_4O_2Ru_2 \cdot 0.75CH_2Cl_2$
M	768.4
Crystal size (mm)	0.20×0.25×0.35
System	monoclinic
Space group	$P2_1/n$
a(Å)	13.302(6)
b(Å)	13.239(7)
c(Å)	18.904(7)
β(deg)	93.75(3)
V(Å^3)	3322.0
Z	4
D_c (g cm^{-3})	1.54
F(000)	1542
Radiation (graphite monochromated (λ, Å)	Mo Kα (0.71067)
μ(Mo Kα) (cm^{-1})	9.94
Diffractometer	Enraf-Nonius CAD4
Scan mode	ω
θ limits (°)	2–25
ω scan width (°)	$0.9+0.35\,\theta$
Prescan rate (deg min^{-1})	5
Prescan acceptance $\sigma(I)/I$	0.5
Required $\sigma(I)/I$	0.02
Maximum scan time (s)	100
Standard reflections	3, measured periodically no decay
Reflections collected	6335
Unique observed reflections $[F_o > 4\sigma(F_o)]$	4844
No. of refined parameters	291
R [a], R_w [b]	0.056, 0.067
$K(g)$ [c]	1.00, 0.0060
Quality of fit indicator [d]	1.24

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$. [c] $w = K/[\sigma^2(F) + |g|F^2]$. [d] Quality of fit $= [\Sigma w(F_o - F_c)^2/(N_{obs} - N_{par})]^{1/2}$.

Table 3
Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for $[Ru_2\{\mu\text{-}C(CN)N(Me)CH_2Ph\}_2(CO)_2Cp_2]$

Atom	x	y	z	U_{iso}
Ru(1)	0.45075(4)	0.14521(3)	0.19506(2)	0.0381(3)
Ru(2)	0.42791(3)	−0.05344(3)	0.20889(2)	0.0361(3)
N(1)	0.2385(4)	0.0647(3)	0.1498(3)	0.042(3)
N(2)	0.4535(4)	0.0648(4)	0.3500(3)	0.044(3)
N(3)	0.3681(5)	0.0249(6)	0.0071(3)	0.066(4)
N(4)	0.6885(5)	0.0258(7)	0.3009(4)	0.077(5)
O(21)	0.2860(4)	0.2224(4)	0.2787(3)	0.066(3)
O(22)	0.2542(4)	−0.0599(4)	0.3020(3)	0.060(3)
C(1)	0.3476(4)	0.0474(4)	0.1428(3)	0.040(3)
C(2)	0.4951(5)	0.0525(4)	0.2802(3)	0.039(3)
C(3)	0.4895(5)	0.1587(5)	0.3867(3)	0.052(4)
C(4)	0.4292(3)	0.1858(3)	0.4484(2)	0.047(3)
C(5)	0.3262(3)	0.1657(3)	0.4477(2)	0.066(5)
C(6)	0.2708(3)	0.1984(3)	0.5036(2)	0.084(6)
C(7)	0.3185(3)	0.2511(3)	0.5602(2)	0.083(6)
C(8)	0.4215(3)	0.2712(3)	0.5609(2)	0.065(4)
C(9)	0.4769(3)	0.2385(3)	0.5051(2)	0.052(4)
C(10)	0.4760(6)	−0.0222(6)	0.3968(3)	0.057(4)
C(11)	0.6028(5)	0.0382(5)	0.2902(4)	0.053(4)
C(12)	0.3631(5)	0.0333(5)	0.0677(3)	0.048(4)
C(13)	0.1759(5)	−0.0245(5)	0.1256(3)	0.048(3)
C(14)	0.0692(2)	−0.0145(3)	0.1442(2)	0.046(3)
C(15)	−0.0073(2)	−0.0472(3)	0.0956(2)	0.059(4)
C(16)	−0.1077(2)	−0.0411(3)	0.1123(2)	0.079(6)
C(17)	−0.1317(2)	−0.0022(3)	0.1777(2)	0.073(5)
C(18)	−0.0553(2)	0.0304(3)	0.2264(2)	0.063(4)
C(19)	0.0452(2)	0.0243(3)	0.2096(2)	0.054(4)
C(20)	0.2035(5)	0.1541(5)	0.1098(4)	0.057(4)
C(21)	0.3478(5)	0.1889(5)	0.2484(3)	0.045(3)
C(22)	0.3193(5)	−0.0539(4)	0.2659(4)	0.045(3)
C(23)	0.5679(6)	0.1623(4)	0.1110(4)	0.051(1)
C(24)	0.6121(6)	0.1946(4)	0.1776(4)	0.051(1)
C(25)	0.5567(6)	0.2792(4)	0.2000(4)	0.051(1)
C(26)	0.4783(6)	0.2991(4)	0.1473(4)	0.051(1)
C(27)	0.4852(6)	0.2269(4)	0.0923(4)	0.051(1)
C(34)	0.6051(13)	0.1640(13)	0.1495(13)	0.051(1)
C(35)	0.5338(13)	0.1823(13)	0.0917(13)	0.051(1)
C(36)	0.4782(13)	0.2702(13)	0.1074(13)	0.051(1)
C(37)	0.5152(13)	0.3062(13)	0.1749(13)	0.051(1)
C(38)	0.5936(13)	0.2406(13)	0.2009(13)	0.051(1)
C(28)	0.4869(6)	−0.1410(5)	0.1166(2)	0.051(1)
C(29)	0.4167(6)	−0.2023(5)	0.1504(2)	0.051(1)
C(30)	0.4554(6)	−0.2200(5)	0.2211(2)	0.051(1)
C(31)	0.5495(6)	−0.1696(5)	0.2310(2)	0.051(1)
C(32)	0.5690(6)	−0.1207(5)	0.1665(2)	0.051(1)
C(39)	0.5167(17)	−0.1994(16)	0.2362(7)	0.051(1)
C(40)	0.5782(17)	−0.1369(16)	0.1959(7)	0.051(1)
C(41)	0.5290(17)	−0.1245(16)	0.1275(7)	0.051(1)
C(42)	0.4371(17)	−0.1793(16)	0.1256(7)	0.051(1)
C(43)	0.4295(17)	−0.2256(16)	0.1928(7)	0.051(1)
Cl(1)	0.9543(7)	0.0969(7)	0.4291(5)	0.202(3)
Cl(2)	0.7724(6)	0.1033(7)	0.5079(4)	0.194(3)
C(33)	0.8313(11)	0.1529(16)	0.4329(9)	0.171(9)

3.9. X-Ray diffraction studies

Crystal data and experimental details for $[Ru_2(CO)_2(Cp)_2\{\mu\text{-}C(CN)N(Me)Bz\}_2] \cdot 0.75CH_2Cl_2$ are given in Table 2. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer. The unit cell parameters were determined from a list of 25 randomly selected strong reflections by using automatic search, indexing and least-squares routines. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied by using the azimuthal scan method [14]. All calculations were performed using the SHELX-76 package of programs [15]. The metal atom positions were determined by direct methods and all non-hydrogen atoms located from difference Fourier syntheses.

The presence of CH_2Cl_2 in the crystal was revealed by the difference Fourier syntheses. An occupation factor was refined for the molecule and converged at 0.75 with isotropic thermal factors for non-hydrogen atoms. Both the phenyl and the cyclopentadienyl rings were treated as rigid groups (C—C, 1.395 and 1.42 Å, respectively). Orientational disorder of the C_5H_5 ligands was detected and site occupation factors were refined independently for the two ligands yielding the values 0.73 and 0.27 (for atoms C(23)—C(27) and C(34)—C(38)), 0.74 and 0.26 (for atoms C(28)—C(32) and C(39)—C(43)). The hydrogen atoms were added in calculated positions (C—H, 1.08 Å) and their coordinates were not refined but continuously updated with respect to their carbon atoms.

The structure model was refined by full matrix least-squares calculations, thermal motion being treated anisotropically for all the non-hydrogen atoms except the cyclopentadienyl C atoms, which were refined with a common isotropic thermal parameter for each ring, and the disordered solvent atoms. The hydrogen atoms were assigned fixed thermal parameters of 0.08 $Å^2$. The final difference-Fourier map showed no features of chemical interest, the largest peaks being around the disordered CH_2Cl_2 molecule (± 1.2 e $Å^{-3}$) and in proximity of the Ru atoms. Positional and equivalent isotropic thermal parameters with their estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table 3 and full lists have been deposited at the Cambridge Crystallographic Data Centre.

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