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# Further investigations on C–C bond formation at the diruthenium aminocarbyne complexes $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, $CH_2Ph$) and molecular structure of $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(COPh)(CO)(Cp)_2]$

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**Abstract**

The reactions of $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me **1a**, $CH_2Ph$ **1b**; Cp = $\eta\text{-}C_5H_5$) with $Li_2Cu(CN)R'_2$ (R′ = Me, $Bu^n$, Ph) result in C–C bond formation at the CO ligand affording the acyl complexes $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(COR')(CO)(Cp)_2]$ **2**. The crystal structure of $[Ru_2\{\mu\text{-}CNMe_2)(\mu\text{-}CO)(COPh)(CO)(Cp)_2]$ **2a** reveals the double bond character of the $\mu$-C=N group and the interligand interaction involving the acyl oxygen and the $\mu\text{-}CNMe_2$ moiety. Type **2** complexes are also formed by reacting **1a**–**b** with LiR′ (R′ = Me, $Bu^n$, Ph), whereas reactions with $ClMgCH_2Ph$ yield both $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(COCH_2Ph)(CO)(Cp)_2]$ and $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(\eta^4\text{-}C_5H_5CH_2Ph)(Cp)]$. A comparison of the reactivity of **1a**–**b** with that of the corresponding diiron complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ is also presented. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Ruthenium; C–C bond formation; Crystal structure; Carbyne complexes

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## 1. Introduction

In the course of the investigations on the selective C–C bond formation at heteroatom-substituted diiron carbyne complexes, we have found that the aminocarbyne derivatives of the type $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, $CH_2Ph$; Cp = $\eta\text{-}C_5H_5$) react with carbon nucleophiles ($R'^-$) to give $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}COR')(CO)_2(Cp)_2]$ or $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(\eta^4\text{-}C_5H_5R')(Cp)]$ via selective addition at the carbonyl (organocuprates, acetylides) and at the cyclopentadienyl ligand (organolithium or Grignard reagents), respectively [1]. The results of analogous reactions of the related $[Fe_2(\mu\text{-}CX)(\mu\text{-}CSMe)(CO)_2(Cp)_2]SO_3CF_3$ (X = O, S) have highlighted the role of the $NR_2$ group in preventing the addition of the carbanions at the bridging carbon of the aminocarbyne ligand [2]. With the aim of extending these studies, as well as to investigate the influence of the nature of the metal atoms, we have focused our attention on the C–C bond forming reactions on the diruthenium derivatives $[Ru_2\{\mu\text{-}CN(R)Me\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, **1a**; $CH_2Ph$, **1b**). Synthetic procedures to generate **1b** and its reaction with $CN^-$ that afford $[Ru_2\{\mu\text{-}C(CN)N(R)Me\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ by addition at the bridging carbyne carbon have been previously described [3]. In this paper we report on the reaction of **1a**–**b** with organomagnesium, -copper and -lithium, which give addition at the CO or Cp ligands. The X-ray crystallographic study of $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(COPh)(CO)(Cp)_2]$ **2a** has established the molecular structure of the acyl derivative.

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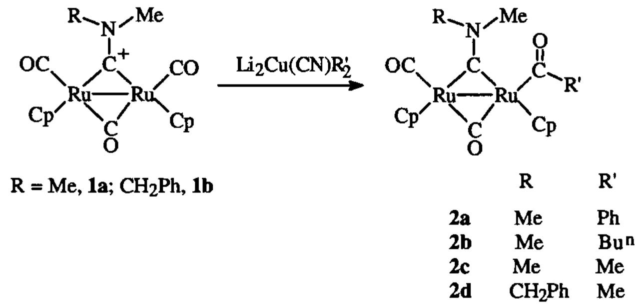


Scheme 1.

## 2. Results and discussion

The reaction of compounds **1a**–**b**, in THF at −40°C, with $Li_2Cu(CN)R'_2$, freshly generated from Cu(CN) and LiR′, affords the acyl complexes $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(COR')(CO)(Cp)_2]$ **2a**–**d** (Scheme 1), which have been isolated in moderately good yields after column chromatography.

The above reactions of **1a**–**b** parallel those of the corresponding diiron aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(R)Me\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, $CH_2Ph$) that have been recently reported [1]. In both cases, the organocopper selectively attacks the CO ligand, yielding acyl derivatives. These similarities, although predictable, are not obvious because complexes **1a**–**b** and their diiron analogues [4] have shown different behaviours in some cases. For example, both **1b** [3] and $[Fe_2\{\mu\text{-}CN(R)Me\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, $CH_2Ph$) [4] undergo hydride addition at the μ-C carbon, transforming the CN(Me)R into the aminocarbene ligand {C(H)N(Me)R}. This grouping is found bridging the two Ru atoms in $[Ru_2\{\mu\text{-}C(H)N(CH_2Ph)Me\}(\mu\text{-}CO)(CO_2)(Cp)_2]$, but terminally coordinated in the diiron complexes. Moreover, the μ-CN(Me)R can be regenerated from the corresponding carbene ligands only in the diiron systems [5].

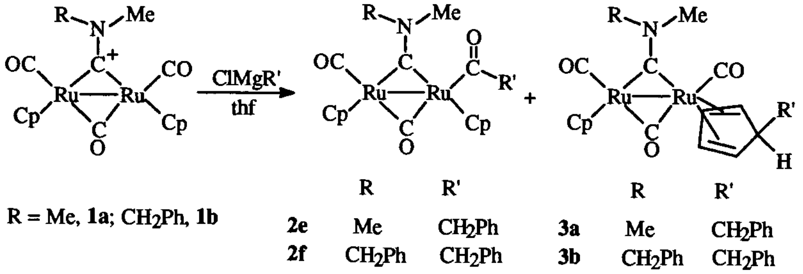
Complexes **2a**–**d** have been characterised by elemental analyses and IR and NMR spectroscopy. An X-ray crystallographic study of **2a** has unambiguously ascertained the molecular structure of the acyl complex (see later).

The IR spectra of **2a**–**d** in $CH_2Cl_2$ solution exhibit one terminal and one bridging carbonyl absorptions (e.g. for **2a** at 1963 and 1773s $cm^{-1}$, respectively) and a ν-(COR) band at ca. 1600 $cm^{-1}$. Evidence of the π-interaction between the carbyne carbon and the adjacent N atom is given by the IR spectra [ν(C=N) absorptions in the 1530–1570 $cm^{-1}$ range] and by the short C–N distance [1.300(4) Å] directly determined in the X-ray diffraction study of **2a**. The non-equivalent Cp groups of **2a**–**c** generate two distinct signals, of the same intensity, in both the $^1H$- and $^{13}C$-NMR spectra (e.g. for **4a** at δ 5.09, 5.20 and δ 90.5, 88.1 ppm, respectively). Likewise, each of the N-bonded methyl groups in **2a**–**c** give rise to a singlet resonance (e.g. for **2a** at 3.90 and 3.84 ppm). An exchange of the methyl groups by rotation around the μ-C–N bond is not allowed because of its double bond character. Major features in the $^{13}C$-NMR spectra of type **2** complexes include the expected low-field resonances of the aminocarbyne carbon, at ca. 305 ppm, and the signal attributable to the acyl carbon around 240 ppm.

Two isomeric forms are observed in the NMR spectra of **2d**, which differ from **2a**–**c** in having the asymmetrically N-substituted $\mu\text{-}CN(Me)CH_2Ph$ ligand in place of the $\mu\text{-}CNMe_2$. These isomeric forms, generally indicated as α and β forms, are usually found in related complexes of the type $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(L)(Cp)_2]$ (R = Et [6], $CH_2Ph$ [1]) and are generated by the different orientation of R and R′ with respect to the non-equivalent Fe atoms.

By contrast with the selective attack of organocopper nucleophiles to the CO ligand of **1a**–**b**, the corresponding treatment with $PhCH_2MgCl$ affords a mixture of the acyl complexes $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(COCH_2Ph)(CO)(Cp)_2]$ **2e**–**f** and the cyclopentadiene complexes $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(\eta^4C_5H_5CH_2Ph)(CO)_2(Cp)]$ **3a**–**b** (Scheme 2), which have been separated by column chromatography. The characterisation of **2e**–**f** has been straightforward since their IR and NMR spectra closely resemble those of the related complexes **2a**–**d** (see Section 3).

The spectroscopic properties of **3a**–**b** are similar to those of the corresponding diiron complexes recently



Scheme 2.

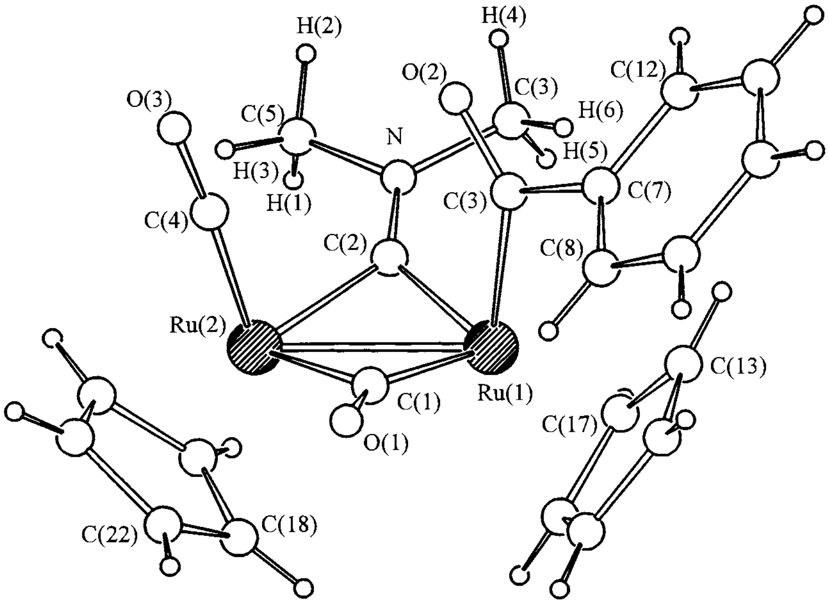


Fig. 1. Molecular structure of $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(COPh)(Co)(Cp)_2]$ (**2a**).

reported [1]. Thus, like $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(\eta^4\text{-}C_5H_5CH_2Ph)(Cp)]$, compound **3a** exhibits in its $^{13}C$-NMR spectrum five distinct resonances for the non-equivalent $C_5H_5R'$ ring carbons (e.g. for **3a** at 92.1, 89.4, 61.9, 61.3, 59.8). The two N-bonded methyl groups are non-equivalent and generate two singlet signals in the $^1H$-NMR spectrum (3.72 and 3.68 ppm).

The reactions of **1a**–**b** with $PhCH_2MgCl$ are less selective compared with those of the diiron complexes. In fact, while $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ ($R = Me, CH_2Ph$) exclusively yield the cyclopentadiene derivatives $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(\eta^4\text{-}C_5H_5CH_2Ph)(CO)_2(Cp)]$, the complexes **1a**–**b** undergo nucleophilic attack at both the CO and Cp ligands. The formation of type **2** complexes suggests that the diruthenium system is more reactive at the CO ligand compared with the diiron counterpart, as confirmed by the reactions with LiR′ (R′ = Me, Bu, Ph). Compounds **1a**–**b** react yielding the acyl derivatives **2** in low yields, whereas treatment of $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ with LiR′ is known to selectively form Cp addition products [1].

Although not directed to the formation of C–C bond, the reaction of **1a**–**b** with NaOMe has also been studied in order to determine whether the carbyne or the CO ligand was preferentially attacked. Like most of the carbon nucleophiles examined above, methoxyde addition occurs at the coordinated CO ligand, affording the alkoxycarbonyl complex $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)\{C(O)OMe\}(CO)(Cp)_2]$ ($R = Me$, **4a**; $CH_2Ph$, **4b**), which have been spectroscopically characterised.

Finally, it is worth mentioning that, unlike $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)\{C(O)OR'\}(CO)(Cp)_2]$ complexes that are known to undergo migration of the COOR′ group to the bridging carbyne carbon [7], compounds **4a**–**b** do not exhibit any migration of the COOMe group.

### *2.1. The molecular structure of $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(COPh)(CO)(Cp)_2]$ **2a***

The molecular structure of **2a** is shown in Fig. 1 and relevant bond lengths and angles are reported in Table 1. The molecule contains two Ru(Cp) units linked together through one μ-CO, one aminocarbyne μ-$CNMe_2$ unit and a direct metal–metal interaction. One CO and one C(O)Ph group are bonded in a mutual *cis* position to Ru(2) and Ru(1), respectively. The molecular geometry of $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}(COPh)(Co)(Cp)_2]$

Table 1

Selected bond lengths (Å) and angles (°) for $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)Ph\}(Cp)_2]$

| | | | |
|---|---|---|---|
| Bond lengths (Å) | | | |
| Ru(1)–Ru(2) | 2.690(1) | N–C(6) | 1.462(6) |
| Ru(1)–C(2) | 1.938(3) | Ru(2)–C(4) | 1.846(4) |
| Ru(2)–C(2) | 1.991(3) | C(4)–O(3) | 1.146(5) |
| Ru(1)–C(1) | 1.944(3) | Ru(1)–C(3) | 2.052(3) |
| Ru(2)–C(1) | 2.168(3) | C(3)–C(7) | 1.515(4) |
| C(1)–O(1) | 1.168(4) | Ru(1)–C(cp) | 2.298 |
| C(2)–N | 1.300(4) | Ru(2)–C(cp) | 2.266 |
| C(5)–N | 1.457(6) | | |
| Bond angles (°) | | | |
| C(4)–Ru(2)–C(2) | 89.0(2) | Ru(1)–C(3)–O(2) | 126.3(3) |
| C(3)–Ru(1)–C(2) | 85.2(1) | Ru(1)–C(1)–O(1) | 148.4(3) |
| C(2)–N–C(5) | 122.7(4) | Ru(2)–C(1)–O(1) | 129.8(2) |
| C(2)–N–C(6) | 121.5(4) | Ru(1)–C(2)–N | 138.8(3) |
| C(5)–N–C(6) | 115.7(4) | Ru(2)–C(2)–N | 134.7(3) |
| Ru(1)–C(3)–C(7) | 118.0(2) | O(2)–C(3)–C(7) | 115.7(3) |

closely resembles that of the iron derivative [$Fe_2(\mu$-$CNMe_2)(\mu$-CO)(CO){C(O)$Bu^n$}$(Cp)_2$] [1]. The idealised $C_s$ symmetry of the parent cation **1a** is violated by the presence of the acyl C(O)Ph group replacing one terminal CO ligand. The molecule is therefore chiral, because the two metal centres are no longer equivalent, but the racemic mixture is present in the crystal. The Ru–Ru interaction [2.690(1) Å] is a bit shorter than the corresponding distances found in *trans*-[$Ru_2(\mu$-$CO)_2$ $(CO)_2(Cp)_2$] (2.738(1) Å) [8], [$Ru_2(\mu$-C(CN)N(Me) $CH_2Ph)(\mu$-$CO)(CO)_2(Cp)_2$] (2.711(1) Å) [3], [$Ru_2(\mu$-$CMe)(\mu$-$CO)(CO)_2(Cp)_2]^+$ (2.714(1) Å) [9], and is very close to the value reported for the $\mu$-vinylidene complex [$Ru_2(\mu$-$CCH_2)(\mu$-$CO)(CO)_2(Cp)_2$] (2.696(1) Å) [9]. If the Ru–Ru distances are compared with the Fe–Fe values found for the iron analogues [2.504(1) Å in [$Fe_2(\mu$-CO)$(\mu$-$CNMe_2$)(CO){C(O)$Bu^n$}$(Cp)_2$] [1] and 2.509(2) Å in $Fe_2${$\mu$-CN(Me)$CH_2Ph$}($\mu$-CO){C(O)th} $(Cp)_2$] [2] (th = $SC_4H_3$)], the increment is perfectly in line with that of the metallic radii (1.26 and 1.34 Å for Fe and Ru, respectively) [10]. The Ru–C bond lengths of the central $Ru_2(\mu$-$C)_2$ diamond, which is folded along the Ru–Ru vector (dihedral angle 29.0(2)°), are highly asymmetric [Ru(1)–C(1) 1.944, Ru(2)–C(1) 2.168, Ru(1)–C(2) 1.938 and Ru(2)–C(2) 1.991(3) Å] the shorter distances being those involving Ru(1) to which the acyl group C(O)Ph is coordinated. This asymmetry in the $Ru_2(\mu$-$C)_2$ unit can be explained in terms of an increased $\pi$ back-donation from Ru(1) to the suitable orbitals of the bridgehead carbons. The charge accumulation on the metal centre Ru(1) that promotes higher back-bonding from this atom is determined by the poor $\pi/\sigma$ ratio of the formally anionic ligand C(O)Ph, in comparison with the CO ligand on Ru(2). The Ru(1)–Ru(2)–C(2) and C(5)–N–C(6) planes are nearly coincident (dihedral angle 5.0(3)°, thus favouring the electron delocalisation in the $Ru_2$–$\mu$-$CNMe_2$ flat grouping. The $\mu$-C–N distance (1.300(4) Å) falls in the range (1.28–1.30 Å) [11] expected for a C=N double bond established by an iminium nitrogen. This interpretation is in accord with the short values observed for the N–C(Me) interactions [N–C(5) 1.457 and N–C(6) 1.462(6) Å] caused by some shrinking of the iminium nitrogen orbitals. Noteworthy the acyl group C(O)Ph is oriented with the oxygen pointing towards the bridging iminium group, with which short contacts are established [O(2)···N, 3.13; O(2)···C(2), 2.78; O(2)···C(6), 3.31 Å]. Similar contacts have been found in the related diiron aminoalkylidyne complexes [$Fe_2(\mu$-CO)$(\mu$-$CNMe_2$)(CO){C(O)$Bu^n$}$(Cp)_2$] [1] and [$Fe_2${$\mu$-CN(Me)$CH_2Ph$}($\mu$-CO){C(O)th}$(Cp)_2$] (th = $SC_4H_3$) [2]. A comparison of the angles between C(2)–Ru(1)–C(3) and C(2)–Ru(2)–C(4) [85.2 and 89.0(2)°, respectively] shows a lower value for the former pertaining to the acyl ligand and therefore, an attractive interaction between the acyl oxygen O(2) and the iminium moiety must be at work. An explanation of this intramolecular interaction, put forward for [$Fe_2(\mu$-CO)$(\mu$-$CNMe_2$) (CO){C(O)$Bu^n$}$(Cp)_2$] [1] on the basis of extended Hückel calculations, is that the negative charge located on the acyl oxygen O(2) and the positive charge distributed around the iminium nitrogen give rise to an interligand attraction [1].

The phenyl ring and the Ru(1), C(3), O(2), C(7) grouping are not coplanar (dihedral angle 51.1(1)°), and no $\pi$-delocalisation is possible, as is also demonstrated by the normal C(acyl)–C(phenyl) bond length (C(3)–C(7) 1.515(4) Å).

## 3. Experimental

### 3.1. General

All reactions were carried out routinely under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Glassware was oven-dried before use. IR spectra were recorded on a Perkin-Elmer 983-G spectrophotometer, $^1H$- and $^{13}C$-NMR spectra on a Varian Gemini 300. The shiftless relaxation reagent [$Cr(acac)_3$] (acac = acetylacetonate) was added to solutions studied by $^{13}C$-NMR spectroscopy. All the reagents were commercial products (Aldrich) of the highest purity available and used as-received. [$Ru_2(CO)_4(Cp)_2$} was from Strem and used as-received. Compounds [$Ru_2${$\mu$-CN(R)Me}($\mu$-$CO)(CO)_2(Cp)_2$] $SO_3CF_3$ (R = Me, **1a**; $CH_2Ph$, **1b**). were prepared from the corresponding isocyanide complexes [3,12]. $Li_2Cu(CN)R_2$ species were prepared from CuCN and the appropriate organolithium reagent according to the literature [13].

### 3.2. Synthesis of [$Ru_2(\mu$-$CNMe_2)(\mu$-CO)(COPh)(CO)$(Cp)_2$] **2a**

Compound **1a** (100 mg, 0.161 mmol) in THF (10 ml) at −30°C was treated with $Li_2Cu(CN)Ph_2$ prepared from dry CuCN (0.018 g, 0.2 mmol) and LiPh (0.4 mmol) in THF (4 ml) at −60°C. The mixture was then warmed to 0°C, stirred for an additional hour and filtered on an alumina pad. Removal of the solvent and chromatography on an alumina column with $CH_2Cl_2$ as eluent gave a yellow fraction, which afforded yellow crystals of **2a** (38 mg, 43%). Analysis. Found: C, 48.12; H, 4.00%. $C_{22}H_{21}NO_3Ru_2$ requires: C, 48.08; H, 3.85%. IR ($CH_2Cl_2$) $\nu_{max}(cm^{-1})$ 1968s, 1785m, 1593m (CO) and 1573m, (C=N). NMR: $\delta_H$ ($CDCl_3$): 7.36–7.18 (5H, m, Ph); 5.20 (5H, s, Cp), 5.09 (5H, s, Cp), 3.90 (3H, s, NMe) and 3.84 (3H, s, NMe) ppm. $\delta_C$ ($CDCl_3$): 306.7 ($\mu$-C), 251.4 ($\mu$-CO), 241.8 (*C*OPh); 201.8 (CO), 155.3, 127.7, 127.1, 124.4 (Ph), 90.5, 88.1 (Cp), 52.1 and 50.4 (Me) ppm.

### *3.3. Synthesis of [Ru$_2$(μ-CNMe$_2$)(μ-CO)(COBu$^n$)(CO)(Cp)$_2$]* **2b**

Complex **2b** was obtained following the same procedure described for the synthesis of **2a**, by reacting **1a** (170 mg, 0.27 mmol) in THF (10 ml) at −10°C, with a slight excess of Li$_2$Cu(CN)Bu$^n_2$ (0.32 mmol). Yield (65 mg, 45%). Analysis. Found: C, 45.32; H, 4.79%. C$_{20}$H$_{25}$NO$_3$Ru$_2$ requires: C, 45.36; H, 4.76%. IR (CH$_2$Cl$_2$) $\nu_{max}$ (cm$^{-1}$) 1960vs, 1781m, 1607m (CO) and 1565mw (C=N). NMR: $\delta_H$ (CDCl$_3$): 5.24 (5H, s, Cp), 5.17 (5H, s, Cp), 3.86 (3H, s, NMe), 3.80 (3H, s, NMe), 2.69–2.36 (2H, m, COC*H*$_2$(CH$_2$)$_2$CH$_3$); 1.29–1.03 (4H, m, COCH$_2$(C*H*$_2$)$_2$CH$_3$); 0.79 (3H, t, $J = 7.0$ Hz, COCH$_2$(CH$_2$)$_2$C*H*$_3$). $\delta_C$ (CDCl$_3$): 305.2 (μ-C), 253.6 (μ-CO), 241.5 (*C*OBu$^n$); 202.6 (CO), 90.2, 87.8 (Cp), 51.9, 50.0 (Me); 62.2, 26.9, 22.2, 14.0 (Bu$^n$).

### *3.4. Synthesis of [Ru$_2$(μ-CNMe$_2$)(μ-CO)(COMe)(CO)(Cp)$_2$]* **2c**

Complex **2c** was obtained following the same procedure described for the synthesis of **2a**, by reacting **1a** (85 mg, 0.137 mmol) in THF (10 ml) at −30°C, with a slight excess of Li$_2$Cu(CN)Me$_2$ (0.15 mmol). Yield (35 g, 52%). Analysis. Found: C, 42.02; H, 3.99%. C$_{17}$H$_{19}$NO$_3$Ru$_2$ requires C, 41.89; H, 3.93%. IR (CH$_2$Cl$_2$) $\nu_{max}$ (cm$^{-1}$) 1960s, 1781m, 1603m (CO) and 1559m, (C=N). NMR: $\delta_H$ (CDCl$_3$): 5.25 (5H, s, Cp), 5.17 (5H, s, Cp), 3.84 (3H, s, NMe), 3.80 (3H, s, NMe) 2.18 (3H, s, COMe); $\delta_C$ (CDCl$_3$): 305.3 (μ-C), 252.4 (μ-CO), 241.3 (*C*OMe); 202.8 (CO), 90.4, 87.9 (Cp), 51.9, 50.0 (NMe) and 49.1 (CO*Me*).

### *3.5. Synthesis of [Ru$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(COMe)(CO)(Cp)$_2$]* **2d**

Complex **2d** was obtained following the same procedure described for the synthesis of **2a**, by reacting **1b** (100 mg, 0.14 mmol) in THF (15 ml) at −40°C, with Li$_2$Cu(CN)Me$_2$ (0.18 mmol). Yield (52 mg, 66%). Analysis. Found: C, 49.01; H, 4.17%. C$_{23}$H$_{23}$NO$_3$Ru$_2$ requires C, 49.02; H, 4.11%. IR (CH$_2$Cl$_2$) $\nu_{max}$ (cm$^{-1}$) 1960vs, 1787s, 1606m (CO) and 1533mw, (C=N). NMR: $\delta_H$ (CDCl$_3$): (α isomer) 7.50–7.30 (5H, m, Ph), 5.43 (1H, d, $J = 14.6$ Hz, C*H*$_2$Ph), 5.35 (1H, d, $J = 14.6$ Hz, C*H*$_2$Ph), 5.22 (5H, s, Cp), 5.17 (5H, s, Cp), 3.65 (3H, s, NMe), 2.20 (3H, s, COMe); (β isomer) 7.50–7.30 (10H, m, Ph), 5.71 (1H, d, $J = 16$ Hz, C*H*$_2$Ph), 5.24 (1H, d, $J = 16$ Hz, C*H*$_2$Ph), 5.31 (5H, s, Cp), 5.13 (5H, s, Cp), 3.67 (3H, s, NMe) and 2.25 (3H, s, COMe); α:β isomers ratio = 0.7.

### *3.6. Syntheses of [Ru$_2$(μ-CNMe$_2$)(μ-CO)(COCH$_2$Ph)(CO)(Cp)$_2$]* **2e** *and [Ru$_2$(μ-CNMe$_2$)(μ-CO)(CO)$_2$(Cp)(C$_5$H$_5$CH$_2$Ph)]* **3a**

Freshly prepared PhCH$_2$MgCl (0.16 mmol) in THF solution (3 cm$^3$) was added to a solution of **1a** (170 mg, 0.27 mmol) in THF (10 cm$^3$) at −10°C. The mixture was then allowed to warm to r.t., stirred for an additional 30 min and filtered on a celite pad. Removal of the solvent and chromatography on an alumina column, with CH$_2$Cl$_2$/petroleum ether 1:1 (v/v) as eluent, gave first a yellow fraction of **3a** (32 mg, 21%). Analysis. Found: C, 49.01; H, 4.17%. C$_{23}$H$_{23}$NO$_3$Ru$_2$ requires C, 49.02; H, 4.11%. IR (CH$_2$Cl$_2$ $\nu_{max}$ (cm$^{-1}$) 1968vs, 1934s, 1785m (CO) and 1554m, (C=N), NMR: $\delta_H$ (CDCl$_3$): 7.28–6.76 (5H, m, Ph), 5.08 (5H, s, Cp), 4.94, 4.58, 3.84, 3.66, 3.15 (5H, m, C$_5$*H*$_5$CH$_2$Ph), 3.72, 3.68 (6H, s, NMe), 2.06–2.00 (2H, m, C*H*$_2$Ph); $\delta_C$ (CDCl$_3$): 253.8 (μ-CO), 202.1, 200.5 (CO), 139.5, 128.9, 127.9, 125.3 (Ph), 92.1, 89.4, 61.9, 61.3, 59.8 (*C*$_5$H$_5$CH$_2$Ph), 87.1 (Cp), 52.6, 52.5, 52.0 (*C*H$_2$Ph and N*Me*$_2$).

Further elution gave a second yellow fraction of **2e** (40 mg, 26%). Analysis. Found: C, 48.94; H, 4.10%. C$_{23}$H$_{23}$NO$_3$Ru$_2$ requires C, 49.02; H, 4.11%. IR (CH$_2$Cl$_2$) $\nu_{max}$ (cm$^{-1}$) 1960s, 1780m, 1615m (CO) and 1565m, (C=N). NMR: $\delta_H$ (CDCl$_3$): 7.39–7.96 (5H, m, Ph), 5.19, 5.18, (10H, s, Cp), 3.86 (1H, d, $J = 14.9$ Hz, C*H*$_2$Ph), 3.78 (1H, d, $J = 14.9$ Hz, C*H*$_2$Ph), 3.87 (3H, s, NMe), 3.79 (3H, s, NMe); $\delta_C$ (CDCl$_3$): 304.8 (μ-C), 249.6 (μ-CO), 242.0 (*C*OCH$_2$Ph); 202.2 (CO), 137.0, 129.5, 127.9, 125.4 (Ph), 90.1, 88.1 (Cp), 68.3 (*C*H$_2$Ph), 52.2 and 50.2 (Me).

### *3.7. Syntheses of [Ru$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(COCH$_2$Ph)(CO)(Cp)$_2$]* **2f** *and [Ru$_2${μ-CN(Me)CH$_2$Ph}(μ-CO)(CO)$_2$(Cp)(C$_5$H$_5$CH$_2$Ph)]* **3b**

The complexes **2f** and **3b** were obtained following the same procedure described for the synthesis of **2e** and **3a**, by reacting **1b** (110 mg, 0.16 mmol) in THF (10 ml) at r.t. with a slight excess of PhCH$_2$MgCl (0.20 mmol).

**2f** (34 mg, 33%). Analysis. Found: C, 54.50; H, 4.25%. C$_{29}$H$_{27}$NO$_3$Ru$_2$ requires C, 54.45; H, 4.25%. IR (CH$_2$Cl$_2$) $\nu_{max}$ (cm$^{-1}$) 1959s, 1781m, 1610m (CO) and 1599m, (C=N). NMR: $\delta_H$ (CDCl$_3$): α isomer 7.50–6.97 (10H, m, Ph), 5.25–5.00 (2H, m, NC*H*$_2$Ph), 5.24, 5.23 (10H, s, Cp), 3.91 (1H, d, $J = 14.91$ Hz, C(O)CH$_2$Ph), 3.81 (1H, d, $J = 14.91$ Hz, C(O)C*H*$_2$Ph), 3.74 (3H, s, NMe); β isomer 7.50–6.97 (10H, m, Ph), 5.47 (1H, d, $J = 15.05$ Hz, NC*H*$_2$Ph), 5.34 (1H, d, $J = 15.05$ Hz, NC*H*$_2$Ph), 5.12, 5.07 (10H, s, Cp), 3.88 (1H, d, $J = 15.06$ Hz, C(O)C*H*$_2$Ph), 3.77 (1H, d, $J = 15.06$ Hz, C(O)C*H*$_2$Ph) and 3.67 (3H, s, NMe), α/β isomer ratio

= 1.2; $\delta_C$ ($CDCl_3$) α and β isomer 307.3, 306.8 (μ-C), 249.6, 248.3 (μ-CO), 241.5, 240.4 ($COCH_2Ph$), 202.4, 201.9 (CO), 136.8–125.3 (Ph), 90.1, 88.0 (Cp), 69.5, 68.1, 67.8, 67.5 ($CH_2Ph$), 49.7 and 47.3 (NMe).

**3b** (32 mg, 31%). Analysis. Found: C, 54.48; H, 4.24%. $C_{29}H_{27}NO_3Ru_2$ requires C, 54.45; H, 4.25%. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1966 vs, 1934m, 1802s (CO) and 1533mw (C=N). NMR: $\delta_H$ ($CDCl_3$): α isomer 7.50–6.90 (10H, m, Ph), 5.42–5.10 (2H, m, $NCH_2Ph$), 5.13 (5H, s, Cp), 5.01, 4.71, 3.80, 3.68, 3.22 (5H, m, $C_5H_5CH_2Ph$), 3.54 (3H, s, NMe) and 1.95 (2H, m, $CH_2Ph$); β isomer: 7.50–6.90 (10H, m, Ph), 5.42–5.10 (2H, m, $NCH_2Ph$), 5.03 (5H, s, Cp), 5.01, 4.63, 3.80, 3.68, 3.02 (5H, m, $C_5H_5CH_2Ph$), 3.55 (3H, s, NMe) and 2.05 (2H, m, $CH_2Ph$); α/β isomer ratio = 1.8.

### *3.8. Reactions of **1a–b** with LiR′ to form **2a**, **2b**, **2d***

Methyllithium (0.06 ml, 1.6 M in $Et_2O$) was added to a stirred solution of **1b** (64 mg, 0.09 mmol) in THF (15 ml) at −40°C. The reaction mixture was then warmed to r.t. and the solvent removed under reduced pressure. Chromatography of the residue on an alumina column, with a $CH_2Cl_2$:hexane mixture (1:2, v:v) as eluent, yielded **2d** (22 mg, 44%).

Complexes **2a** (10% yield) and **2b** (12% yield) were prepared by the same procedure above described, by reacting **1a** with LiPh and LiBu$^n$, respectively.

### *3.9. Synthesis of [$Ru_2$(μ-$CNMe_2$)(μ-CO){C(O)OMe}(CO)(Cp)$_2$] **4a***

Sodium methoxide (0.30 mmol) was added to a solution of **1a** (180 mg, 0.29 mmol) in THF (20 ml) at −40°C. The mixture was stirred for 30 min, allowed to warm to r.t. and filtered through a celite pad. The volatile material was removed in vacuo and the residue was redissolved in $CH_2Cl_2$, layered with pentane and crystallised at −20°C affording **4a** in ca. 41% yield. Analysis. Found: C, 40.42; H, 3.87%. $C_{19}H_{19}NO_4Ru_2$ requires C, 40.55; H, 3.80%. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1965vs, 1792s, 1615m (CO) and 1559mw (C=N). NMR: $\delta_H$ ($CDCl_3$): 5.23 (5H, s, Cp), 5.18 (5H, s, Cp), 3.81 (3H, s, NMe), 3.79 (3H, s, NMe), 3.19 (3H, s, COMe).

### *3.10. Synthesis of [$Ru_2${μ-CN(Me)($CH_2Ph$}(μ-CO){C(O)OMe}(CO)(Cp)$_2$] **4b***

The complex **4b** was obtained following the same procedure described for the synthesis of **4a** by reacting **1b** (100 mg, 0.14 mmol) with NaOMe. Yield 32%. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1963vs, 1809s, 1621m (CO) and 1537mw (C=N). NMR: $\delta_H$ ($CDCl_3$) (α + β isomers): 7.48–7.22 (5H, m, Ph), 5.53 (1H, d, $J$ = 15 Hz, $CH_2Ph$), 5.35 (1H, d, $J$ = 15 Hz, $CH_2Ph$), 5.30, 5.25, 5.17, 5.16 (10H, s, Cp), 3.68, 3.66 (3H, s, NMe), 3.24 and 3.23 (3H, s COMe).

Table 2
Crystal data and experimental details for [$Ru_2$(μ-$CNMe_2$)(μ-CO)(CO){C(O)Ph}(Cp)$_2$]

| | |
|---|---|
| Formula | $C_{22}H_{21}NO_3Ru_2$ |
| $M$ | 549.54 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71069 |
| Crystal symmetry | Monoclinic |
| Space group | $P2_1/c$ (No. 14) |
| $a$ (Å) | 15.198(6) |
| $b$ (Å) | 7.326(1) |
| $c$ (Å) | 18.621(4) |
| $\beta$ (°) | 105.42(2) |
| $V$ (Å$^3$) | 1998.6(9) |
| $Z$ | 4 |
| $D_{calc}$ (Mg m$^{-3}$) | 1.826 |
| $\mu$(Mo–K$_\alpha$) (mm$^{-1}$) | 1.534 |
| $F$(000) | 1088 |
| Crystal size (mm) | 0.10 × 0.125 × 0.40 |
| $\theta$ limits (°) | 2.5–30 |
| Scan mode | $\omega$ |
| Reflections collected | 5988($\pm h$, $+k$, $+l$) |
| Unique observed reflections [$F_0 > 4\sigma(F_0)$] | 5761 |
| Goodness-of-fit on $F^2$ | 1.024 |
| $R_1$ ($F$)$^a$, $wR_2$ ($F^2$)$^b$ | 0.0304, 0.0798 |
| Weighting scheme $a$, $b$ | 0.0446, 2.4884$^b$ |
| Largest difference peak and hole eÅ$^{-3}$ | 1.080 and −0.614 |

[a] $R_1 = \Sigma||F_0| - |F_c|/\Sigma|F_0|$.

[b] $wR_2 = [\Sigma\, w(F_0^2 - F_c{}^2)^2/\Sigma\, w(F_0{}^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_0{}^2) + (aP)^2 + bP]$ where $P = (F_0{}^2 + 2F_c{}^2)/3$.

### *3.11. X-ray structure determination of [$Ru_2$(μ-$CNMe_2$)(μ-CO)(COPh)(CO)(Cp)$_2$]*

The diffraction experiments were carried out at r.t. on a fully automated CAD4 diffractometer. The unit cell parameters were determined by a least-squares fitting procedure using 25 reflections. Crystal data and details of the data collection for the title compound are given in Table 2. Intensity data were corrected for Lorentz and polarisation effects. No decay correction was necessary. The metal atom positions were determined by direct methods using SHELXS 86 [14]. Least-squares refinement and Fourier difference syntheses revealed all remaining non-H atoms. All the hydrogen atoms were located from successive Fourier difference maps but were added in calculated positions as the cyclopentadienyl hydrogen atoms. Two-fold orientational disorder of both the Cp ligands around the metal–ring axes was detected and the site occupation factors were refined for these ligands, yielding the values 0.54 and 0.46 [for atoms C(13)–C(17) and C(28)–C32)] and 0.64 and 0.36 [for atoms C(18)–C(22) and C(23)–C(27)]. The final refinement on $F^2$ proceeded by full-matrix least-squares calculations (SHELXL 93 [15])

Table 3
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)Ph\}(Cp)_2]$

| Atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Ru(1) | 7192(1) | 1788(1) | 147(1) | 31(1) |
| Ru(2) | 8109(1) | 862(1) | 1543(1) | 37(1) |
| C(1) | 6824(2) | 24(5) | 791(2) | 35(1) |
| O(1) | 6264(2) | −960(4) | 893(1) | 53(1) |
| C(2) | 8482(2) | 1753(4) | 657(2) | 37(1) |
| N | 9256(2) | 2162(5) | 525(2) | 50(1) |
| C(5) | 10121(3) | 2095(9) | 1098(3) | 80(2) |
| C(6) | 9312(4) | 2676(9) | −220(3) | 81(2) |
| C(4) | 8558(3) | −1414(6) | 1403(2) | 52(1) |
| O(3) | 8860(2) | −2830(5) | 1359(2) | 82(1) |
| C(3) | 7476(2) | −451(4) | −415(2) | 37(1) |
| O(2) | 8208(2) | −1251(4) | −293(2) | 57(1) |
| C(7) | 6734(1) | −1149(3) | −1073(1) | 40(1) |
| C(8) | 5872(2) | −1606(4) | −1004(1) | 51(1) |
| C(9) | 5233(1) | −2380(4) | −1603(2) | 66(1) |
| C(10) | 5455(2) | −2696(4) | −2270(1) | 79(2) |
| C(11) | 6316(2) | −2239(4) | −2338(1) | 76(1) |
| C(12) | 6956(2) | −1465(4) | −1739(1) | 58(1) |
| C(13) | 6701(4) | 3519(8) | −868(3) | 47(1) |
| C(14) | 5914(3) | 2775(7) | −703(3) | 47(1) |
| C(15) | 5854(3) | 3517(8) | −13(3) | 47(1) |
| C(16) | 6604(5) | 4718(7) | 248(2) | 47(1) |
| C(17) | 7127(3) | 4720(7) | −280(4) | 47(1) |
| C(23)* | 6410(4) | 3154(8) | −932(2) | 47(1) |
| C(24)* | 5807(3) | 2975(8) | −470(4) | 47(1) |
| C(25)* | 6151(4) | 4064(9) | 175(3) | 47(1) |
| C(26)* | 6966(4) | 4915(7) | 111(3) | 47(1) |
| C(27)* | 7126(3) | 4353(9) | −573(4) | 47(1) |
| C(18) | 7547(4) | 3139(7) | 2145(3) | 52(1) |
| C(19) | 8509(5) | 3340(6) | 2304(3) | 52(1) |
| C(20) | 8919(2) | 1745(8) | 2682(3) | 52(1) |
| C(21) | 8210(4) | 557(5) | 2757(3) | 52(1) |
| C(22) | 7362(2) | 1419(9) | 2425(3) | 52(1) |
| C(28)* | 7385(4) | 2074(17) | 2378(5) | 52(1) |
| C(29)* | 7887(9) | 3481(11) | 2141(5) | 52(1) |
| C(30)* | 8826(7) | 2998(13) | 2364(5) | 52(1) |
| C(31)* | 8904(4) | 1292(14) | 2737(6) | 52(1) |
| C(32)* | 8014(7) | 721(11) | 2746(6) | 52(1) |

* C(28)–C(32) and C(23)–C(27) are the minor components of the disordered cyclopentadienyl rings bound to Ru(1) and Ru(2), respectively.

using anisotropic thermal parameters for all the non-hydrogen atoms except the cyclopentadienyl C atoms. The H atoms were assigned an isotropic thermal parameter 1.2 times $U_{eq}$ of the carbon atoms to which they were attached. The final Fourier difference map was featureless. Final positional parameters with their estimated S.D. are given in Table 3. A complete list of bond lengths and angles and a table of anisotropic displacement parameters has been deposited at the Cambridge Crystallographic Data Centre.

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