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Ruthenium complexes with bridging functionalized alkylidene ligands. Synthesis of $[Ru_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(X)N(Me)CH_2Ph\}]$ (X = H, CN) and molecular structure of the CN derivative

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Abstract

The isocyanide complex $[Ru_2Cp_2(CO)_3(CNCH_2Ph)]$, obtained by the reaction of $[Ru_2Cp_2(CO)_4]$ with $CNCH_2Ph$ in the presence of Me_3NO, has been N-alkylated, yielding the cationic μ-alkylidyne complex $[Ru_2Cp_2(CO)_3\{\mu\text{-}CN(Me)CH_2Ph\}]SO_3CF_3$. The compound yielded undergoes nucleophilic addition using $NaBH_4$ or N^nBu_4CN at the μ-C alkylidyne carbon to give the novel μ-aminoalkylidene complexes $[Ru_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(X)N(Me)CH_2Ph\}]$ (X = H, CN). The derivative with X = CN adopts the expected geometry and an idealized C_s symmetry if the phenyl substituent is ignored. The relevant bond distances are as follows: Ru–Ru, 2.711(1) Å; Ru–μ-C(carbene), 2.090(4) Å (ave.); C(carbene)–N, 1.477(5) Å; N–C(alkyl), 1.474(5) Å (ave.).

1. Introduction

Several synthetic routes to diruthenium μ-alkylidene complexes have been reported. Significant examples include the treatment of $[Ru_2Cp_2(CO)_4]$ with organolithium, $HBF_4 \cdot OEt_2$ and $NaBH_4$ [1], and reactions of $[Ru_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}]$ with diazoalkanes [2], ylides [2], alkynes [3] and allenes [4]. However, none of these reactions can be simply directed to heteroatom-substituted bridging alkylidene, which is found in a poorly explored class of compounds [5]. Since we recently succeeded in the preparation of a variety of stable diiron μ-aminoalkylidene complexes [6], we have become interested in the chemistry of the unknown ruthenium analogues. Indeed, our synthesis of $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(X)CN(R)COSR\}]$ through stepwise N-alkylation and X^- (X = CN, H) addition at the μ-C of the functionalized isocyanide $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNCOSR)]$ [7] suggested a convenient entry. Here, we report the successful extension of this method to the isocyanide complex $[Ru_2Cp_2(CO)_3(CNCH_2Ph)]$, which has been obtained from $[Ru_2Cp_2(CO)_4]$ by Me_3NO-promoted CO substitution with $CNCH_2Ph$. The X-ray molecular structure of the novel μ-aminoalkylidene $[Ru_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)N(Me)CH_2Ph\}]$ is discussed.

2. Results and discussion

The reaction of $[Ru_2Cp_2(CO)_4]$ with isocyanides in refluxing xylenes is known to form $[Ru_2Cp_2(CO)_3(CNR)]$ (R = Me, Et, ^iPr, ^tBu) [8]. However, the same method extended to $CNCH_2Ph$ gave a poor yield (less than 10%) of the expected $[Ru_2Cp_2(CO)_3(CNCH_2Ph)]$ (**1**). We have found that this complex can be more conveniently prepared using Me_3NO-induced CO substitution in $[Ru_2Cp_2(CO)_4]$. The reaction in refluxing tetrahydrofuran for 24 h formed the desired isocyanide **1** (30% yield) together with comparable amounts of the disubstituted $[Ru_2Cp_2(CO)_2(CNCH_2Ph)_2]$ (**2**) (27%).

The isocyanide derivatives were separated by column chromatography and characterized from their ^1H NMR and IR spectroscopic data. In solution in

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CH_2Cl_2, they do not exhibit absorptions in the 2000–2200 cm^{-1} range where the terminally coordinated CNR ligands are expected to absorb. This observation is consistent with the tendency of the isocyanide ligands towards bridging in diruthenium complexes [8]. By analogy with $[M_2Cp_2(CO)_3CNR]$ (M = Fe, Ru) [7–9], complex **1** readily reacts with $MeSO_3CF_3$ in the CH_2Cl_2 solution, to form the bright yellow $[Ru_2Cp_2(CO)_3\{\mu\text{-}CN(Me)CH_2Ph\}]^+$ (**3**) (Scheme 1). The spectroscopic properties of complex **3**, which indicate the presence of bridging $CN(Me)CH_2Ph$ (ν(CN) at 1595 cm^{-1}), suggest the *cis* geometry (terminal CO groups on the same side of the molecule) usually found for the analogous Fe and Ru cationic complexes. Moreover, the unequivalence of the Cp groups, as indicated by the two badly resolved, equally intense resonances at δ 5.71 and 5.72 in the ^1H NMR spectrum, suggests hindered rotation around the C=N bond.

We recently suggested that the μ-C=N(R)(R′) moiety in cationic diiron derivatives is better if regarded as an aminoalkylidyne rather than as an iminium bridging ligand [7]. The reaction of **3** with nucleophiles confirms our view. Addition of CN^- or H^- to the μ-C of the aminoalkylidyne ligand in **3** yields the aminoalkylidene complexes $[Ru_2Cp_2(CO)_3\{\mu\text{-}C(X)N(Me)CH_2Ph\}]$ (X = CN, **4a**; H, **4b**) (Scheme 1).

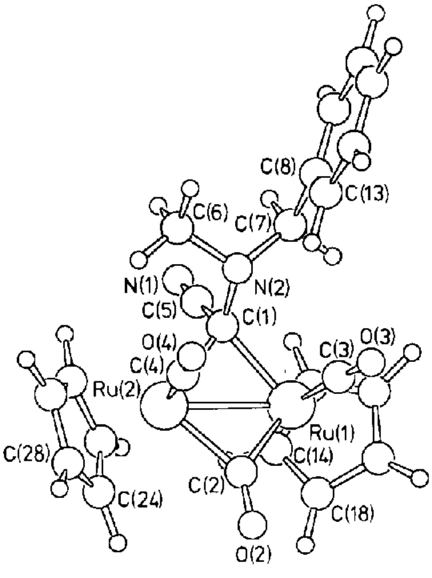
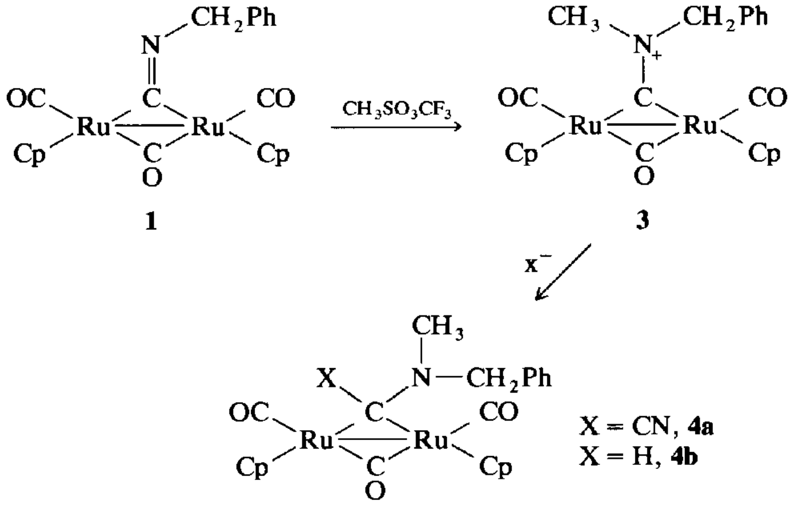


Fig. 1.

The spectroscopic properties of complexes of type **4** are consistent with the structure of the cyanide adduct **4a**, as established by X-ray crystallography (Fig. 1). The IR ν(CO) band pattern in type **4** derivatives is similar to that of their precursor **3** (*e.g.* 2006vs, 1950m, 1806s for **4a**), though shifted to somewhat lower wavenumbers, indicating that they also are *cis* in solution. Moreover, the occurrence of one single Cp resonance in both ^1H (δ 5.30 for **4a**) and ^{13}C (δ 93.2 for **4a**) NMR spectra indicates only one *cis* isomer which, according to the molecular structure of **4a**, is that bearing the smaller X substituent on the more hindered Cp side of the molecule.

The ^{13}C NMR spectra of **4a** show several signals in the δ 150–120 region, where the resonances of the CN group, the μ-alkylidene and the aromatic carbons are expected. In order to assign correctly the bridging carbene carbon, a sample of **4a** was prepared by the reaction of **3** with a mixture of $K[^{13}CN]$ and N^nBu_4CN. Enrichment in ^{13}C isotope (30%) was evaluated approximately by the IR ν(CN) absorption for the ^{13}CN in **4a** at 2102 cm^{-1} in CH_2Cl_2. The ^{13}C NMR spectrum run on a ^{13}C-enriched sample allowed an unam-



Scheme 1.

TABLE 1. Selected bond lengths and angles for **4a**

	Bond length (Å)		Angle (°)
Ru(1)–Ru(2)	2.711(1)	Ru(1)–C(3)–O(3)	175.6(4)
Ru(1)–C(1)	2.087(4)	Ru(2)–C(4)–O(4)	177.1(4)
Ru(2)–C(1)	2.093(4)	Ru(1)–C(2)–O(2)	136.8(4)
Ru(1)–C(2)	2.044(4)	Ru(2)–C(2)–O(2)	139.4(4)
Ru(2)–C(2)	2.025(4)	C(1)–C(5)–N(1)	177.0(4)
C(2)–O(2)	1.176(5)	Ru(1)–C(1)–Ru(2)	80.9(1)
Ru(1)–C(3)	1.856(5)	C(2)–Ru(1)–Ru(2)	47.9(1)
Ru(2)–C(4)	1.867(4)	C(2)–Ru(1)–C(1)	95.5(2)
C(3)–O(3)	1.142(5)	Ru(1)–C(2)–Ru(2)	83.6(2)
C(4)–O(4)	1.139(5)	C(7)–N(2)–C(6)	110.0(3)
C(1)–C(5)	1.471(5)	C(5)–C(1)–N(2)	109.4(3)
C(5)–N(1)	1.143(5)	C(7)–N(2)–C(1)	110.9(3)
C(1)–N(2)	1.477(5)	C(6)–N(2)–C(1)	112.4(3)
N(2)–C(6)	1.474(5)		
N(2)–C(7)	1.473(5)		
C(7)–C(8)	1.538(4)		
Ru(1)–C(cp) (ave.)	2.272		
Ru(2)–C(cp) (ave.)	2.264		

biguous identification of the CN (at δ 127.7) and μ-C resonances (at δ 139.5). The μ-C resonance also shows satellite peaks owing to the C–C coupling (J(C–C) = 41 Hz). The remaining resonances at δ 140.5, 129.0, 128.9 and 127.5 were assigned to the phenyl-ring carbons.

2.1. *Molecular structure of [$Ru_2Cp_2(CO)_2$(μ-CO){μ-C(CN)N(Me)CH_2Ph}] (4a)*

The crystal structure of the complex [$Ru_2Cp_2(CO)_2$(μ-CO){μ-C(CN)N(Me)CH_2Ph}] (**4a**) consists of isolated molecules separated by normal van der Waals' interactions. A perspective view of the molecular structure with its atomic numbering scheme is shown in Fig. 1, and the bond lengths and angles are listed in Table 1. The molecule contains the dimeric unit $\{Ru(Cp)CO\}_2$ in the *cis* configuration with a metal–metal bond. The metal–metal interaction is strengthened by two bridging groups: CO and the functionalized alkylidene group C(CN)N(Me)CH_2Ph. The molecular geometry has an idealized C_s symmetry if the phenyl substituent is ignored. Actually, the amine nitrogen N(2) is a chiral centre but the crystal is racemic. The coordination geometry around the Ru atom is pseudo-octahedral and the two metal atoms are chiral centres of opposite configuration. The Ru–Ru distance (2.711(1) Å) is strictly comparable with the value found in the related alkylidene complexes [$Ru_2Cp_2(CO)_2$(μ-CO)(μ-CMe_2)] [4] and [$Ru_2Cp_2(CO)_2$(μ-CO)(μ-CH_2)] [2], *i.e.* 2.712(1) Å and 2.701(1) Å respectively. It is some 0.18 Å longer than the average Fe–Fe value in the analogous diiron complexes (2.53 Å) [6,7,10]. As expected on the basis of molecular orbital calculations on [$M_2Cp_2(CO)_4$] [11] and as found in analogous diruthenium species [2,4], the Ru_2(μ-C$)_2$ unit is non-planar. The dihedral angle between the Ru(1), Ru(2), C(1) and Ru(1), Ru(2), C(2) planes is 20°, with the two bridging groups bent towards the less hindered terminal CO ligands.

The planar μ-C(CN)N(amine) group lies approximately normal to the Ru(1), Ru(2), C(1) plane (dihedral angle between the Ru(1), Ru(2), C(1) and C(1), C(5), N(2) planes 89°) and the Ru(1)–C(1)–Ru(2) angle is 80.9(1)°. In the complex [$Ru_2Cp_2(CO)_4$(μ-CH_2)] [11], in which an Ru–Ru bond is absent (Ru–Ru 3.8 Å), the Ru–μ-CH_2–Ru angle is 123°; this large value has been attributed to steric crowding. The geometry of the μ-aminoalkylidene group μ-C(CN)N(Me)CH_2Ph in **4a** is comparable with that of the μ-C(CN)N(Me)C(O)SMe in [$Fe_2(CO)_2(Cp)_2$(μ-CO){μ-C(CN)N(Me)C(O)SMe}] [7] (M–μ-C 2.090(4) Å (ave.); 1.993(3) Å (ave.); μ-C–C≡N 1.471(5) Å, 1.143(5) Å, 1.438(5) Å, 1.149(5) Å respectively; μ-C–N(amine) 1.477(5) Å; 1.492(4) Å; C–C(carbene)–N 109.4(3)°; 105.3(3)°; M–C(carbene)–M 80.9(1)°, 77.9(1)°). The small differences are not very significant but the N(2)–C(1)–C(5) angle is wider in the Ru derivative. This happens because the CN ··· H contacts are shorter than in the Fe derivative owing to the tetrahedral hybridization of the N(2) orbitals. Another feature of interest is that the N(amine)–C interactions do not differ in length despite their chemical unequivalence (N(2)–C(1) 1.477(5) Å, N(2)–C(6) 1.474(5) Å, N(2)–C(7) 1.473(5) Å).

3. Experimental details

All the reactions were carried out routinely under dinitrogen by standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. The $CNCH_2Ph$ (Aldrich) was used as received. IR spectra were recorded on a Perkin–Elmer 983-G. NMR spectra were recorded on a Varian Gemini 200 spectrometer. Elemental analyses were determined by Pascher Microanalytical Laboratorium (Remagen, Germany).

3.1. *Synthesis of [$Ru_2Cp_2(CO)_3CNCH_2Ph$] (1) and [$Ru_2Cp_2(CO)_2(CNCH_2Ph)_2$] (2)*

A mixture of [$Ru_2Cp_2(CO)_4$] (1.43 g, 3.22 mmol), benzyl isocyanide (0.56 g, 4.83 mmol) and Me_3NO (48 mg in 5 ml of MeOH) was heated in THF (40 ml) at reflux for 24 h. The solvent was then removed *in vacuo* and the residue chromatographed on an alumina column (3 cm × 10 cm). Elution with CH_2Cl_2 gave a first yellow fraction containing unreacted $[RuCp(CO)_2]_2$ (0.07 g, 5%). A second yellow fraction was collected, evaporated to minimum volume and layered with pentane, giving crystals of [$Ru_2Cp_2(CO)_3CNCH_2Ph$] (0.52 g, 30%). M.p. 170°C–172°C (dec.). Anal. Found: C, 46.9; H, 3.3. $C_{21}H_{17}NO_3Ru_2$ calc.: C, 47.27; H, 3.21%.

IR (CH_2Cl_2): ν(CO) 1995vs, 1953m, 1791s, ν(CN) 1705s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.41–7.25 (m, 5 H, C_6H_5); 5.33 (s, 10 H, Cp); 4.82 (s, 2 H, NCH_2Ph). Finally, a third fraction of $[RuCp(CO)(CNCH_2Ph)]_2$ (**2**) was evaporated to dryness and crystallized from CH_2Cl_2–light petroleum, giving yellow crystals (0.54 g, 27%). M.p. 131°C–133°C (dec.). Anal. Found: C, 54.5; H, 4.2. $C_{28}H_{24}N_2O_2Ru_2$ calc.: C, 54.01; H, 3.88%. IR (CH_2Cl_2): ν(CO) 1988vs, 1948m, ν(CN) 1683s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44–7.30 (m, 10 H, C_6H_5); 5.31 (s, 10 H, Cp); 4.85 (s, 4 H, NCH_2Ph). ^{13}C NMR (CD_2Cl_2): δ 230.8 (μ-CNR); 200.4 (CO); 140.9, 129.1, 127.9, 127.4 (C_6H_5); 89.5 (Cp); 66.4 (NCH_2).

3.2. Synthesis of $[Ru_2Cp_2(CO)_3\{\mu\text{-}CN(Me)CH_2Ph\}]SO_3CF_3$ (3)

A dichloromethane solution (30 ml) of complex **1** (0.38 g, 0.71 mmol) was stirred with a slight excess of $CF_3SO_3CH_3$ (85 μl) for 10 min. The solution was then evaporated to dryness *in vacuo* and the residue washed with Et_2O (3–5 ml) and redissolved in CH_2Cl_2. The addition of Et_2O gave a yellow microcrystalline precipitate of complex **3** (0.36 g, 72%). M.p. 178°C–179°C (dec.). Anal. Found: C, 39.7; H, 3.2. $C_{23}H_{20}F_3NO_6SRu_2$ calc.: C, 39.60; H, 2.89%. IR (CH_2Cl_2): ν(CO) 2025vs, 1992m, 1842s, ν(CN) 1595m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.43–7.30 (m, 5 H, C_6H_5); 5.72, 5.71 (s, 10 H, Cp); 5.62, 5.55 (s, 2 H, NCH_2Ph), 3.82 (s, 3 H, Me).

3.3. Synthesis of $[Ru_2Cp_2(CO)_3\{\mu\text{-}C(CN)N(Me)CH_2Ph\}]$ (4a)

Complex **3** (0.31 g, 0.45 mmol) was allowed to react with a slight excess of N^nBu_4CN (0.12 g, 0.45 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred for 10 min and then filtered through an alumina pad (3 cm × 3 cm). Evaporation of the solvent *in vacuo* and crystallization of the residue from a CH_2Cl_2–light petroleum (b.p. 40°C–60°C) mixture at −20°C gave yellow crystals of **4a** (0.16 g, 63%). M.p. 180°C–181°C (dec.). Anal. Found: C, 48.0; H, 3.8. $C_{23}H_{20}N_2O_3Ru_2$ calc.: C, 48.07; H, 3.51%. IR (CH_2Cl_2): ν(CO) 2006vs, 1970m, 1806s, ν(CN) 2151w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.31–7.20 (m, 5 H, C_6H_5); 5.30 (s, 10 H, Cp); 4.20 (s, 2 H, NCH_2Ph), 2.54 (s, 3 H, Me).

A sample of **4a** enriched with ^{13}CN was prepared by adding $K[^{13}CN]$ (Fluka) (0.01 g, 0.15 mmol) and N^nBu_4CN (0.08 g, 0.30 mmol) to a solution of **3** (0.30 g, 0.45 mmol) in CH_3CN (15 ml). After stirring for 1 h and the usual work-up, a sample of **4a** (0.16 g) suitable for ^{13}C NMR characterization was obtained. ^{13}C NMR (CD_2Cl_2): δ 239.0 (br, μ-CO); 198.0 (br, CO); 139.5 (J(C–C) = 41 Hz, μ-C), 127.7 (CN), 140.5, 129.0, 128.9, 127.5 (Ph); 93.3 (Cp); 65.9 (NCH_2Ph), 45.4 (NMe).

3.4. Synthesis of $[Ru_2Cp_2(CO)_3\{\mu\text{-}C(H)N(Me)CH_2Ph\}]$ (4b)

To a stirred solution of **3** (0.24 g, 0.34 mmol) in CH_3CN (20 ml) was added $NaBH_4$ (25 mg, 0.67 mmol). After 15 min the mixture was reduced in volume and filtered through an alumina column (3 cm × 5 cm) with CH_2Cl_2 as eluent. The yellow solution obtained was evaporated to dryness *in vacuo* and the residue was crystallized from CH_2Cl_2, and layered with pentane at −20°C. Yield 0.11 g, 57%. M.p. 176°C–178°C (dec.). Anal. Found: C, 48.2; H, 4.0. $C_{22}H_{21}NO_3Ru_2$ calc.: C, 48.08; H, 3.85%. IR (CH_2Cl_2): ν(CO) 1955vs, 1918m, 1762s cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.19 (s, 1 H, μ-CH); 7.38–7.24 (m, 5 H, C_6H_5); 5.12 (s, 10 H, Cp); 4.40 (s, 2 H, NCH_2Ph), 2.88 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$, at −60°C): δ 257.3 (μ-CO); 202.4 (CO); 163.3 (μ-C); 138.0, 128.3, 127.7, 127.2 (Ph); 89.5 (Cp); 63.7 (NCH_2Ph); 42.7 (NMe).

TABLE 2. Crystal data and experimental details for $[Ru_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)N(Me)CH_2Ph\}]$ (**4a**)

Formula	$C_{23}H_{20}N_2O_3Ru_2$
M	574.6
Crystal size (mm)	0.125×0.10×0.15
System	orthorhombic
Space group	*Pbca* (no. 61)
a (Å)	12.807(6)
b (Å)	13.705(5)
c (Å)	24.994(6)
V (Å³)	4386.9
Z	8
D_c (g cm^{-3})	1.74
F(000)	2272
Radiation (graphite monochromated (λ, Å)	Mo Kα(0.71067)
μ(Mo Kα) (cm^{-1})	12.62
Diffractometer	Enraf-Nonius CAD4
Scan mode	ω
θ limits (°)	2–25
ω scan width (°)	0.6 + 0.35 tg θ
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	3501
Unique observed reflections $[F_o > 4\sigma(F_o)]$	2738
No. of refined parameters	197
R [a], R_w [b]	0.0249, 0.0289
K (g) [c]	2.11, 5.3×10^{-4}
Quality of fit indicator [d]	1.83

[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 for $[Ru_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(Me)CH_2Ph\}]$ (**4a**)

Atom	x	y	z	U_{eq}
Ru(1)	0.15684(2)	0.16582(2)	0.11325(1)	0.0359(2)
Ru(2)	−0.00874(2)	0.07962(2)	0.16160(1)	0.0327(2)
N(1)	−0.0683(3)	0.1279(3)	0.0092(1)	0.058(2)
N(2)	−0.0521(2)	0.2835(2)	0.1138(1)	0.033(2)
C(1)	−0.0030(3)	0.1881(3)	0.1027(1)	0.034(2)
C(2)	0.1428(3)	0.0913(3)	0.1837(2)	0.045(2)
O(2)	0.1990(3)	0.0641(3)	0.2178(1)	0.074(2)
C(3)	0.1655(3)	0.2787(4)	0.1541(2)	0.051(3)
O(3)	0.1776(3)	0.3479(3)	0.1788(2)	0.080(3)
C(4)	−0.0402(4)	0.1763(3)	0.2117(2)	0.046(2)
O(4)	−0.0616(3)	0.2324(3)	0.2435(1)	0.075(2)
C(5)	−0.0388(3)	0.1519(3)	0.0503(2)	0.037(2)
C(6)	−0.1668(3)	0.2770(3)	0.1169(2)	0.046(2)
C(7)	−0.0214(4)	0.3562(3)	0.0733(2)	0.044(2)
C(8)	−0.0544(2)	0.4591(1)	0.0912(1)	0.037(2)
C(9)	−0.0437(2)	0.4876(1)	0.1444(1)	0.051(3)
C(10)	−0.0668(2)	0.5833(1)	0.1595(1)	0.063(3)
C(11)	−0.1005(2)	0.6504(1)	0.1213(1)	0.064(3)
C(12)	−0.1111(2)	0.6219(1)	0.0680(1)	0.066(3)
C(13)	−0.0881(2)	0.5263(1)	0.0529(1)	0.049(3)
C(14)	0.2095(4)	0.0499(3)	0.0534(2)	0.054(1)
C(15)	0.1938(4)	0.1384(3)	0.0250(2)	0.054(1)
C(16)	0.2648(4)	0.2087(3)	0.0454(2)	0.054(1)
C(17)	0.3243(4)	0.1636(3)	0.0865(2)	0.054(1)
C(18)	0.2901(4)	0.0654(3)	0.0914(2)	0.054(1)
C(19)	0.2614(9)	0.0393(6)	0.0811(4)	0.054(1)
C(20)	0.1904(9)	0.0663(6)	0.0401(4)	0.054(1)
C(21)	0.2083(9)	0.1659(6)	0.0274(4)	0.054(1)
C(22)	0.2905(9)	0.2005(6)	0.0605(4)	0.054(1)
C(23)	0.3233(9)	0.1222(6)	0.0937(4)	0.054(1)
C(24)	0.0040(3)	−0.0837(4)	0.1692(2)	0.046(1)
C(25)	−0.0267(3)	−0.0624(4)	0.1159(2)	0.046(1)
C(26)	−0.1260(3)	−0.0166(4)	0.1177(2)	0.046(1)
C(27)	−0.1567(3)	−0.0095(4)	0.1722(2)	0.046(1)
C(28)	−0.0763(3)	−0.0510(4)	0.2040(2)	0.046(1)
C(29)	−0.0361(6)	−0.0689(7)	0.1979(2)	0.046(1)
C(30)	0.0125(6)	−0.0855(7)	0.1477(2)	0.046(1)
C(31)	−0.0545(6)	−0.0485(7)	0.1072(2)	0.046(1)
C(32)	−0.1444(6)	−0.0090(7)	0.1324(2)	0.046(1)
C(33)	−0.1330(6)	−0.0216(7)	0.1885(2)	0.046(1)

3.5. X-ray diffraction studies

Crystal data and details of the data collection for **4a** are given in Table 2. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. The cell constants were determined from a list of 25 randomly selected strong reflections using automatic search, indexing and least-squares routines. Data were corrected for Lorentz and polarization effects. No decay correction was necessary. All the calculations were performed using the SHELX76 package of programs [12]. The metal atom positions were determined by direct methods and all the non-hydrogen atoms located from difference Fourier syntheses. An empirical absorption correction was applied using the method of Walker and Stuart [13] once the structural model was completely defined and the thermal motion of all the atoms refined isotropically. Both the phenyl and the cyclopentadienyl rings were treated as rigid groups (C–C 1.395 Å and 1.42 Å respectively). The orientational disorder of the C_5H_5 ligands was detected and the site occupation factors were refined independently for the two ligands, yielding the values 0.66 and 0.34 (for atoms C14–C18 and C19–C23), 0.60 and 0.40 (for atoms C24–C28 and C29–C33). 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 final refinement proceeded using anisotropic thermal parameters for all the non-hydrogen atoms except the cyclopentadienyl C atoms which were refined with a common isotropic thermal parameter for each ring. The hydrogen atoms were assigned fixed thermal parameters of 0.08 Å^2. The final difference Fourier map showed peaks not exceeding 0.6 e Å^3. The final positional and equivalent isotropic thermal parameters with their estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table 3.

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