Organic Chemistry of Dinuclear Metal Centres. Part 13.[1] Synthesis, Structure, and Reactivity of [Ru₂(CO)₄(η⁵:η⁵'-C₅H₄CH₂C₅H₄)]†

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Reaction of $[Ru_3(CO)_{12}]$ with bis(cyclopentadienyl)methane in boiling toluene gives $[Ru_2(CO)_4$-$(\eta^5:\eta^{5'}$-$C_5H_4CH_2C_5H_4)]$ (**1**) in good yield. The molecular structure has been determined by X-ray diffraction. The structure was solved by heavy-atom methods and refined by least squares to give a final R 0.045 for 3 009 unique, observed diffractometer data. Crystals of (**1**) are orthorhombic, space group *Pbca*, with $Z = 16$ in a unit cell of dimensions $a = 18.066(9)$, $b = 14.321(6)$, and $c = 22.156(10)$ Å. The molecule consists of a staggered $(OC)_2Ru$–$Ru(CO)_2$ unit bridged by a bis(cyclopentadienylene)methane ligand which is η^5-bound to each ruthenium atom. I.r. spectroscopy reveals that this structure dominates in solution, but that a low concentration of a carbonyl-bridged isomer is also present. Sequential treatment of complex (**1**) with LiMe, tetrafluoroboric acid, and $NaBH_4$ affords the bis-μ-ethylidene complex $[Ru_2(CO)_2(\mu$-$CHMe)_2(\eta^5:\eta^{5'}$-$C_5H_4CH_2C_5H_4)]$ (**7**), the structure of which has also been determined by X-ray diffraction, and solved and refined as above to a final R 0.025 for 1 813 data. Crystals of (**7**) are monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no.14), with $Z = 4$ in a unit cell of dimensions $a = 8.702(3)$, $b = 12.653(4)$, $c = 14.508(6)$ Å, and $\beta = 98.01(3)°$. The molecule contains an $(OC)Ru$–$Ru(CO)$ unit bridged by two ethylidene groups so as to give a highly folded $Ru_2(\mu$-$C)_2$ core. The methyl groups of the ethylidenes are oriented *anti* with respect to a bridging bis(cyclopentadienylene)methane ligand bound in an $\eta^5:\eta^{5'}$ fashion as for complex (**1**). Although the μ-$C \cdots \mu$-C distance in complex (**7**) is relatively short (3.11 Å), thermolysis induces alkylidene linking less efficiently than for related η-C_5H_5 complexes with a non-folded geometry, a difference attributed to the reduced flexibility in (**7**) arising from the coupling of the η-C_5 rings. Reaction of complex (**1**) with $Li[BHEt_3]$–water affords the μ-methylene complex $[Ru_2(CO)_2(\mu$-$CO)(\mu$-$CH_2)(\eta^5:\eta^{5'}$-$C_5H_4CH_2C_5H_4)]$. Photolysis of (**1**) in the presence of diphenylacetylene gives $[Ru_2(CO)_2(\mu$-$CO)(\mu$-$\sigma:\sigma'$-$C_2Ph_2)(\eta^5:\eta^{5'}$-$C_5H_4CH_2C_5H_4)]$, containing a 'parallel' two-electron alkyne ligand. The Ru–Ru bond of (**1**) is cleaved by iodine to yield $[Ru_2I_2(CO)_4(\eta^5:\eta^{5'}$-$C_5H_4CH_2C_5H_4)]$, which is readily converted into $[Ru_2Me_2(CO)_4(\eta^5:\eta^{5'}$-$C_5H_4CH_2C_5H_4)]$ on treatment with $Li[CuMe_2]$.

In earlier papers in this series we have described how the complex $[Ru_2(CO)_4(\eta$-$C_5H_5)_2]$ can be used to establish a substantial organic chemistry of the diruthenium centre. In the complexes which have been derived from this species the cyclopentadienyl ligands are found to adopt both *cis* and *trans* arrangements with respect to the metal–metal bond. While orbital overlap considerations favour the *cis* isomer,[2] steric factors[3] work in favour of the *trans*. The balance is such that the isomers often interconvert, depending on the ease with which bridging ligands can be induced to become terminal and thus allow rotation about the metal–metal bond.[4] In this paper we describe the synthesis of the bis(cyclopentadienylene)methane complex $[Ru_2(CO)_4(\eta^5:\eta^{5'}$-$C_5H_4CH_2C_5H_4)]$ (**1**), an analogue of $[Ru_2(CO)_4(\eta$-$C_5H_5)_2]$ in which, formally, two η-C_5H_5 ligands are linked *via* a methylene bridge. The objective was to explore the effect on the organic chemistry of the diruthenium centre of thus constraining the system to adopt a *cis* configuration. Substantial differences are observed, as described below. Since we first communicated[5] the successful synthesis of (**1**), others[6] have also done so. Complexes in which the di-iron,[6] dicobalt,[7] and dirhodium[8–10] centres are bridged by the μ-η^5: $\eta^{5'}$-$C_5H_4CH_2C_5H_4$ ligand are known.

Results and Discussion

Synthetic Studies.—Some years ago we reported that $[Ru_2$-$(CO)_4(\eta$-$C_5H_5)_2]$ is readily prepared by heating $[Ru_3(CO)_{12}]$ with cyclopentadiene in heptane.[11,12] The same approach is successful for $[Ru_2(CO)_4(\eta^5:\eta^{5'}$-$C_5H_4CH_2C_5H_4)]$ (**1**). Thus, when $[Ru_3(CO)_{12}]$ and a four-fold excess of bis-cyclopenta-dienyl)methane[13] is heated in boiling heptane for 7 h a 56% yield of (**1**) is obtained. An alternative route,[6] in which the olefin is first converted into the dithallium salt, $Tl_2[CH_2(C_5H_4)_2]$, and this is then treated with $[Ru_2Cl_4(CO)_6]$, is much less efficient, affording only a 5% yield of (**1**).

Complex (**1**) is yellow, crystalline, and air-stable. The i.r. spectrum in solution consists of three strong terminal carbonyl absorptions (at 2 014, 1 962, and 1 941 cm⁻¹) and one very weak bridging carbonyl absorption (at 1 780 cm⁻¹), indicating that both isomers (**1a**) and (**1b**) are present (see Scheme), with the former dominant. This contrasts with $[Ru_2(CO)_4(\eta$-$C_5H_5)_2]$, which exists in solution as a more nearly equal mixture of the bridged and non-bridged forms.[14] The reasons for this difference are explained by the results of an X-ray diffraction study on (**1a**), described below. The ¹H n.m.r. spectrum of (**1**) at room temperature reveals the protons of the linking CH_2 group as a singlet and the protons of the C_5H_4 rings as $[AB]_2$ systems. This is in accord with a rapid carbonyl scrambling process[15] which interconverts (**1a**) and (**1b**), and renders the two 'sides' of the bis(cyclopentadienylene) ligand equivalent.
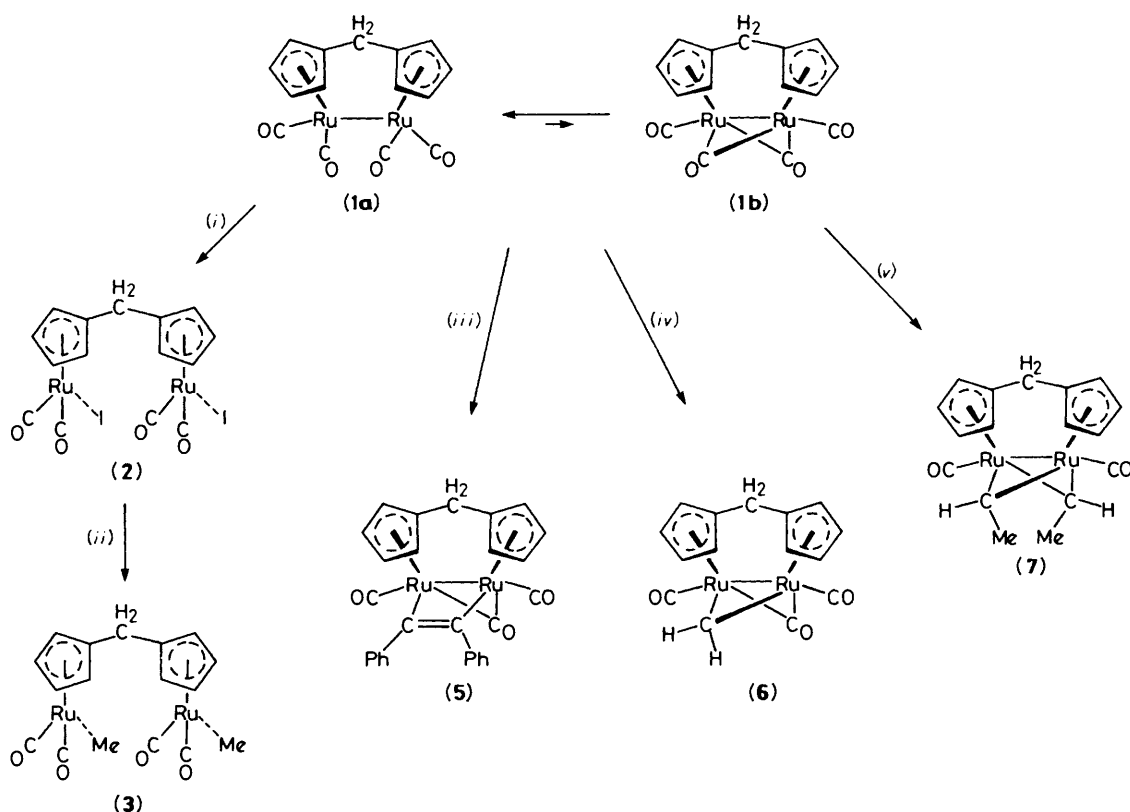
Scheme. (*i*) I$_2$; (*ii*) Li[CuMe$_2$]; (*iii*) PhC$_2$Ph, u.v. irradiation; (*iv*) Li[BHEt$_3$], water; (*v*) LiMe, HBF$_4$, NaBH$_4$

Complex (**1**) displays the same reactivity as [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] towards a halogen. Ruthenium–ruthenium bond cleavage occurs rapidly on treatment with iodine in chloroform, giving [Ru$_2$I$_2$(CO)$_4$(η^5:$\eta^{5'}$-C$_5$H$_4$CH$_2$C$_5$H$_4$)] (**2**) in high yield. The latter is equally easily converted into the dimethyl derivative [Ru$_2$Me$_2$(CO)$_4$(η^5:$\eta^{5'}$-C$_5$H$_4$CH$_2$C$_5$H$_4$)] (**3**) upon reaction with lithium dimethylcuprate. The characterisation of (**2**) and (**3**) was straightforward (see Experimental section). From these simple reactions it is evident that (**1**) can serve as a precursor of a considerable amount of organoruthenium chemistry, paralleling that of [RuX(CO$_2$)(η-C$_5$H$_5$)] species.

The development of the organic chemistry of the diruthenium centre has been greatly assisted by the complex [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$Ph$_2$}(η-C$_5$H$_5$)$_2$] (**4**), which loses diphenyl-

(**4**)
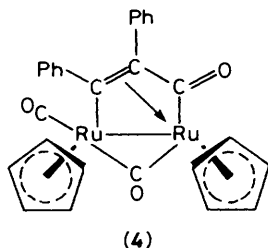
acetylene readily and thus acts as an excellent source of the unsaturated fragment [Ru$_2$(CO)$_3$(η-C$_5$H$_5$)$_2$].[16] Complex (**4**) is prepared by the reaction of [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] with diphenylacetylene under u.v. irradiation,[17] but treatment of (**1**) with the alkyne under the same conditions did not give an analogous species. Instead, a 22% yield of the μ-σ,σ'-alkyne complex [Ru$_2$(CO)$_2$(μ-CO)(μ-σ: σ'-C$_2$Ph$_2$)(η^5: $\eta^{5'}$-C$_5$H$_4$CH$_2$-C$_5$H$_4$)] (**5**) was obtained. The nature of (**5**) was evident from the

i.r. spectrum, which showed the presence of both terminal and bridging CO ligands and the absence of a ketonic CO, and the ^{1}H and ^{13}C n.m.r. spectra, which revealed higher symmetry than that expected for an analogue of (**4**). Unlike (**1**), however, the two 'sides' of the η-C$_5$H$_4$ rings in (**5**) are non-equivalent and the protons of each appear as ABCD rather than [AB]$_2$ patterns. The CH$_2$ protons likewise are seen as an AB quartet rather than a singlet. We have previously observed that the presence of very electronegative substituents on an alkyne is conducive of the μ-σ:σ' ('parallel') mode of bridging, as in [Ru$_2$(CO)$_2$(μ-CO)(μ-σ:σ'-C$_2$R$_2$)(η-C$_5$H$_5$)$_2$] (R = CO$_2$Me[17] or CF$_3$[18]). In the η-C$_5$H$_5$ system diphenylacetylene binds only as in (**4**) or in the μ-η^2:$\eta^{2'}$ ('perpendicular') mode in [Ru$_2$(μ-CO)(μ-η^2:$\eta^{2'}$-C$_2$Ph$_2$)(η-C$_5$H$_5$)$_2$].[16] Parallel diphenylacetylene is, however, present in the μ-fulvalenyl complex [Ru$_2$(CO)$_2$(μ-CO)(μ-σ:σ'-C$_2$H$_2$)(η^5:$\eta^{5'}$-C$_{10}$H$_8$)].[19] Like (**5**) this species has two η^5-C$_5$H$_4$ rings linked together, suggesting that the pinning-back of the rings is influential in the determination of the mode of co-ordination of ligands at the diruthenium centre (see later).

Complex (**5**) is not a useful entry into organodiruthenium chemistry; unlike (**4**), attempted reactions with a variety of reagents did not result in the displacement of the alkyne. Some direct reactions of (**1**) were, however, successful in generating μ-alkylidene complexes. The reaction of (**1**) with Li[BHEt$_3$]–water converts a CO ligand into CH$_2$, in a manner identical to that observed for [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$][20] and [Os$_3$(CO)$_{12}$],[21] giving [Ru$_2$(CO)$_2$(μ-CO)(μ-CH$_2$)(η^5: $\eta^{5'}$-C$_5$H$_4$CH$_2$C$_5$H$_4$)] (**6**) in ca. 30% yield. The behaviour of (**1**) and [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] towards methyl-lithium was found to be different. Whereas the latter reacts with methyl-lithium, tetrafluoroboric acid, and NaBH$_4$, in sequence, to form the mono-μ-ethylidene complex [Ru$_2$(CO)$_2$(μ-CO)(μ-CHMe)(η-C$_5$H$_5$)$_2$],[22] similar treatment of (**1**) gave the di-μ-ethylidene species [Ru$_2$(CO)$_2$(μ-CHMe)$_2$(η^5: $\eta^{5'}$-C$_5$H$_4$CH$_2$C$_5$H$_4$)] (**7**) in 23% yield. Even when
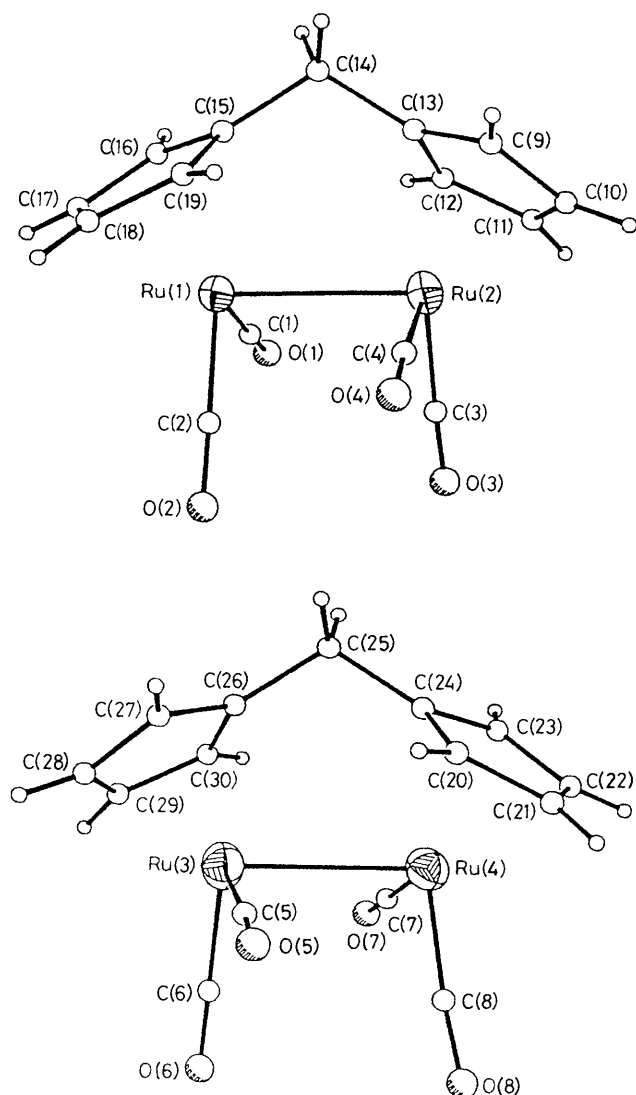
Figure 1. Molecular structure of complex (1a), showing labelling scheme for the two independent molecules present in the crystal structure

Figure 2. Molecular structure of complex (7), showing labelling scheme

a deficiency of methyl-lithium was employed no mono-μ-ethylidene complex was detected, suggesting, surprisingly, that after nucleophilic attack of Me⁻ on a CO ligand of (1) to afford anionic [Ru₂{C(O)Me}(CO)₃(η⁵:η⁵′-C₅H₄CH₂C₅H₄)]⁻ a second Me⁻ attack occurs on a CO of this species in preference to neutral (1). Although, as described in the preceding paper,[1] attempts to obtain a di-μ-ethylidene complex from [Ru₂(CO)₂-(μ-CO)(μ-CHMe)(η-C₅H₅)₂] were unsuccessful, treatment of the μ-CMe₂ analogue with MeLi–HBF₄–NaBH₄ did give [Ru₂(CO)₂(μ-CHMe)(μ-CMe₂)(η-C₅H₅)₂]. It appears that the site of Me⁻ attack in diruthenium carbonyl complexes, and whether it occurs at all, is in very fine balance.

The complexes (6) and (7) were readily identified from their i.r. and n.m.r. spectra (see Experimental section). The alkylidene ligands show the now characteristic low-field n.m.r. signals for μ-CH protons and carbons, while the different symmetry of the two complexes is reflected in the expected ABCD pattern for the ring protons of (6) and the [AB]₂ pattern for the ring protons of (7). It is interesting that a doubly bridged structure is favoured for (6) and (7) whereas, as described earlier, the unbridged structure (1a) is preferred for the parent tetracarbonyl. In order to probe this phenomenon X-ray diffraction studies were undertaken on (1a) and (7). It was also hoped that the structure
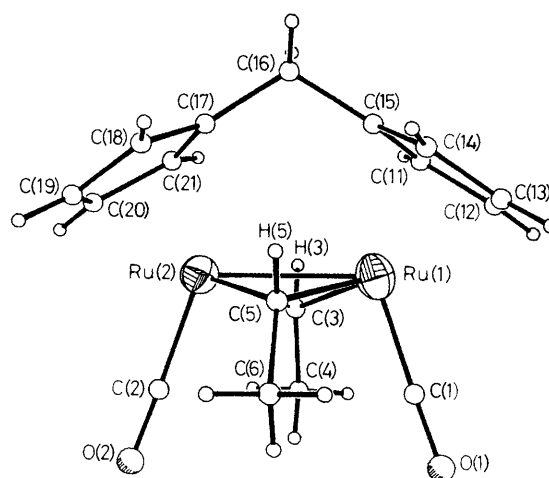
of (1a) would shed light on the alkylidene coupling reaction at a diruthenium centre, a process discussed at length in the preceding paper.[1] Whereas the trans complex [Ru₂(CO)₂(μ-CHMe)(μ-CMe₂)(η-C₅H₅)₂] affords 64% of methylbutenes on heating, only 36% of butenes is evolved from (7) at 230 °C, yet the cis geometry of the latter, and consequently[2] the folded Ru₂(μ-C)₂ core, implies a closer approach of the bridging alkylidene carbons.

Crystal and Molecular Structures of Complexes (1a) *and* (7).—A perspective view of the molecular structure of the two crystallographically independent molecules of complex (1a) is given in Figure 1; bond lengths and inter-bond angles are listed in Table 1. The crystal structure consists of isolated molecules of (1a) separated by normal van der Waals distances. The two independent molecules are chemically identical, showing some minor variations in bond and, especially, torsion angles. Except where noted, molecular dimensions quoted are averaged over the two molecules. Each molecule shows approximate local C_2 symmetry, with the C_2 axis passing through the methylene carbon atom [C(14), C(25)] and the midpoint of the Ru–Ru bond. Molecules of (1a) consist of two ruthenium atoms at a single bond distance [2.766(1) Å], each carrying two terminal carbonyl ligands and bridged by a bis(cyclopentadienylene)-methane (bcpm) ligand which ligates each metal in an η⁵ fashion. The Ru–Ru distance is longer than that in *trans*-[Ru₂(CO)₂(μ-CO)₂(η-C₅H₅)₂] [2.735(2) Å],[23] presumably as a consequence of the lack of bridging ligands in (1a). The carbonyl ligands are staggered relative to one another [the smaller C–Ru–Ru–C torsion angles fall in the range 44.8(4) to 46.6(4)° for the first molecule and 30.8(4) to 58.5(4)° for the second]. This staggering follows from a twist about the Ru–Ru bond and presumably relieves unfavourable non-bonded inter-ligand interactions. The amount of twist is clearly easily varied, as reflected in the difference in cp–Ru–Ru–cp torsion angles between the two independent molecules (39.9 and 49.2°, cp being the centroid of an η-C₅ ring).

A perspective view of the molecular structure of complex (7) is given in Figure 2; bond lengths and inter-bond angles are listed in Table 2. The crystal structure consists of isolated molecules of (7) separated by normal van der Waals distances. The molecules show approximate C_{2v} local symmetry in the solid state with the C_2 axis passing through the midpoint of the Ru–Ru bond and the methylene carbon [C(16)], and one of the mirror planes perpendicular to and bisecting the Ru–Ru bond. The two ruthenium atoms are at a single bond distance [2.634(1) Å], each carrying a single terminal carbonyl ligand, and are bridged

Table 1. Selected bond lengths (Å) and angles (°) for complex (1a)

Ru(1)–Ru(2)	2.767(1)	Ru(1)–C(1)	1.858(8)
Ru(1)–C(2)	1.853(8)	Ru(1)–C(15)	2.268(7)
Ru(1)–C(16)	2.257(8)	Ru(1)–C(17)	2.234(9)
Ru(1)–C(18)	2.248(9)	Ru(1)–C(19)	2.239(8)
Ru(2)–C(3)	1.847(8)	Ru(2)–C(4)	1.840(9)
Ru(2)–C(9)	2.259(8)	Ru(2)–C(10)	2.231(9)
Ru(2)–C(11)	2.228(8)	Ru(2)–C(12)	2.251(7)
Ru(2)–C(13)	2.275(8)	Ru(3)–Ru(4)	2.764(1)
Ru(3)–C(5)	1.858(10)	Ru(3)–C(6)	1.834(9)
Ru(3)–C(26)	2.259(8)	Ru(3)–C(27)	2.235(10)
Ru(3)–C(28)	2.222(12)	Ru(3)–C(29)	2.242(11)
Ru(3)–C(30)	2.248(8)	Ru(4)–C(7)	1.845(9)
Ru(4)–C(8)	1.832(9)	Ru(4)–C(20)	2.258(8)
Ru(4)–C(21)	2.261(9)	Ru(4)–C(22)	2.241(10)
Ru(4)–C(23)	2.243(9)	Ru(4)–C(24)	2.240(7)
C(1)–O(1)	1.141(10)	C(2)–O(2)	1.145(10)
C(3)–O(3)	1.140(11)	C(4)–O(4)	1.155(11)
C(5)–O(5)	1.138(12)	C(6)–O(6)	1.174(11)
C(7)–O(7)	1.149(11)	C(8)–O(8)	1.160(11)
C(9)–C(10)	1.421(12)	C(9)–C(13)	1.384(12)
C(10)–C(11)	1.406(13)	C(11)–C(12)	1.402(12)
C(12)–C(13)	1.430(12)	C(13)–C(14)	1.500(13)
C(14)–H(14a)	0.899(58)	C(14)–H(14b)	1.338(67)
C(14)–C(15)	1.504(12)	C(15)–C(16)	1.413(12)
C(15)–C(19)	1.408(10)	C(16)–C(17)	1.406(12)
C(17)–C(18)	1.380(12)	C(18)–C(19)	1.415(12)
C(20)–C(21)	1.408(12)	C(20)–C(24)	1.408(12)
C(21)–C(22)	1.379(13)	C(22)–C(23)	1.382(13)
C(23)–C(24)	1.436(14)	C(24)–C(25)	1.509(14)
C(25)–C(26)	1.508(15)	C(26)–C(27)	1.391(16)
C(26)–C(30)	1.396(12)	C(27)–C(28)	1.390(17)
C(28)–C(29)	1.378(17)	C(29)–C(30)	1.403(15)
Ru(2)–Ru(1)–C(1)	85.6(3)	Ru(2)–Ru(1)–C(2)	89.5(3)
C(1)–Ru(1)–C(2)	91.8(3)	Ru(1)–Ru(2)–C(3)	91.9(3)
Ru(1)–Ru(2)–C(4)	86.3(3)	C(3)–Ru(2)–C(4)	91.6(4)
Ru(4)–Ru(3)–C(5)	87.8(3)	Ru(4)–Ru(3)–C(6)	93.3(3)
C(5)–Ru(3)–C(6)	89.4(4)	C(7)–Ru(4)–C(8)	88.4(4)
Ru(3)–Ru(4)–C(7)	84.6(3)	Ru(3)–Ru(4)–C(8)	94.7(3)
Ru(1)–C(1)–O(1)	176.7(7)	Ru(1)–C(2)–O(2)	178.6(7)
Ru(2)–C(3)–O(3)	177.9(7)	Ru(2)–C(4)–O(4)	177.7(8)
Ru(3)–C(5)–O(5)	175.5(8)	Ru(3)–C(6)–O(6)	178.4(8)
Ru(4)–C(7)–O(7)	177.8(8)	Ru(4)–C(8)–O(8)	175.0(9)
C(13)–C(14)–C(15)	114.5(7)	C(24)–C(25)–C(26)	114.3(7)

by two μ-ethylidene ligands and a bcpm ligand, bound as in (1a). The two bridging CHMe ligands force the molecule to adopt a geometry in which the carbonyl ligands are mutually eclipsed (C–Ru–Ru–C 0.9°), in contrast to the twisting observed for (1a). The μ-CHMe ligands adopt an *anti* conformation which directs the methyl substituents away from the bcpm ligand, thereby reducing unfavourable non-bonded interactions.

The linkage between the η-C₅ rings confers a *cis* geometry on the Ru₂(η-C₅)₂ skeletons of both (1a) and (7), and in contrast to related species the ring carbons are forced into proximity by the linking methylene {shortest C ⋯ C approaches are 2.527 and 2.534 Å for the two molecules of (1a) and 2.534 Å for (7); cf. 3.722 Å in cis-[Ru₂(CO)₂(μ-CO)(μ-CMe₂)(η-C₅H₅)₂]⁵}. As a result the C₅ ring planes in (1a) and (7) are inclined to one another at a shallower angle than is usually the case (ca. 90°) in cis-Ru₂(η-C₅)₂ species {interplanar angles are 112.9 and 115.7° for (1a) and (7) respectively; cf. 90.7° in cis-[Ru₂(CO)₂(μ-CO)(μ-CMe₂)(η-C₅H₅)₂]⁴}. This pinning-back of the η-C₅ rings requires a highly folded Ru₂(μ-C)₂ core if the diruthenium centre is to be doubly bridged, as is typically the case for Ru₂L₄(η-C₅)₂ species. Excessive folding of this type would be expected to be disfavoured on orbital overlap grounds.² It seems, therefore, that the highly folded, doubly bridged

geometry will be adopted when the bridging ligands strongly prefer bridging over terminal sites, as is the case for alkylidenes, in (7), but not for carbonyls, in (1a). The degree of folding in (7) is indicated by the angle between the Ru₂(μ-C) planes {31.3°; cf. values in the range 15—27° for cis-[Ru₂(CO)₂(μ-CO)(μ-L)(η-C₅H₅)₂] [L = CMe⁺,²² CH₂,²⁴ CCH₂,²² or CMe₂⁴]}. In the case of [Ru₂(CO)₄(η⁵: η⁵'-C₁₀H₈)], the even shallower inter-C₅ plane angle (151.5°) causes an all-terminal arrangement for the carbonyl ligands, and an even longer Ru–Ru distance [2.821(1) Å].¹⁹

The folding in the core of complex (7) leads to a relatively short μ-C ⋯ μ-C distance {3.11 Å; cf. 3.20 Å in trans-[Ru₂(CO)₂(μ-CHMe)(μ-CMe₂)(η-C₅H₅)₂]¹}. Although this might be expected to lead to a more facile alkylidene linking reaction, the observation that pyrolysis of (7) gives smaller yields of coupling products than does pyrolysis of trans-[Ru₂(CO)₂(μ-CHMe)(μ-CMe₂)(η-C₅H₅)₂] indicates that other factors must be taken into account. The most likely factor is the reduced flexibility of (7) arising from the coupling of C₅ rings in the bcpm ligand.

Experimental

G.l.c. (gas–liquid chromatography) analysis of hydrocarbon products was carried out on a Pye Series 104 instrument, employing a 2-m Chromosorb 102 column (80–100 mesh) operating at 114 °C with a nitrogen carrier gas flow rate of 40 cm³ min⁻¹. Diphenylacetylene, NaBH₄, HBF₄·OEt₂, and Li[BHEt₃] were used as supplied by Aldrich, and methyl-lithium by Ventron. Bis(cyclopentadienyl)methane was prepared by the literature method.¹³

Preparations.—[Ru₂(CO)₄(η⁵: η⁵'-C₅H₄CH₂C₅H₄)] (1). A mixture of [Ru₃(CO)₁₂] (4.8 g, 7.5 mmol) and bis(cyclo-pentadienyl)methane (4 g, 27.8 mmol) in heptane (350 cm³) was heated under reflux for 7 h. Solvent was then removed under reduced pressure and the residue introduced to an alumina column in the minimum of dichloromethane. Elution with hexane developed a yellow band which contained some unreacted [Ru₃(CO)₁₂] and oily organic residues. A second yellow band, removed with hexane–dichloromethane (3:2), gave a yellow solution which upon evaporation afforded 2.9 g (56%) of yellow crystalline (1) [m.p. 174—176 °C (decomp.); (Found: C, 39.7; H, 2.2%; M 457; C₁₅H₁₀O₄Ru₂ requires C, 39.5; H, 2.2%; M 457); ν(CO) (in CH₂Cl₂) at 2 014s, 1 962m, 1 941m, and 1 780w cm⁻¹; ¹H n.m.r. (in CDCl₃) δ 5.38, 4.97 (8 H, 2 C₅H₄, [AB]₂ system), and 3.71 (s, 2 H, CH₂); ¹³C-{¹H} n.m.r. (in CDCl₃) δ 22.7 (CH₂), 85.2 (8 CH of C₅H₄), 94.2 (CCH₂), and 206.4 (CO)], further purified by recrystallisation from hexane–dichloromethane.

[Ru₂(CO)₂(μ-CHMe)₂(η⁵:η⁵'-C₅H₄CH₂C₅H₄)] (7). Methyl-lithium (2 cm³ of a 1 mol dm⁻³ solution in diethyl ether) was added to a solution of complex (1) (0.215 g, 0.47 mmol) in thf (tetrahydrofuran) and the mixture was stirred at room temperature for 0.5 h. The solution was then cooled to −78 °C, an excess (ca., 1 cm³) of HBF₄·OEt₂ was added, and the mixture was stirred for 10 min then allowed to warm to room temperature. An excess of NaBH₄ (0.25 g, 6.6 mmol) was then added and the mixture stirred for a further 0.5 h. Solvent was then evaporated under reduced pressure and the residue extracted with portions of dichloromethane which were then washed through a short alumina column. Subsequent chromatography, eluting with hexane–dichloromethane (4:1), gave a yellow band from which 48 mg (23%) of yellow crystalline (7) was obtained [m.p. 261–263 °C (decomp.) (Found: C, 43.9; H, 4.1%; M 457 C₁₇H₁₈O₂Ru₂ requires C, 44.7; H, 4.0%; M 457); ν(CO) (in CH₂Cl₂) at 1 948s and 1 917m cm⁻¹; ¹H n.m.r. (in

Table 2. Selected bond lengths (Å) and angles (°) for complex (7)

Ru(1)–Ru(2)	2.634(1)	Ru(1)–C(1)	1.828(5)
Ru(1)–C(3)	2.083(4)	Ru(1)–C(5)	2.083(5)
Ru(1)–C(11)	2.292(5)	Ru(1)–C(12)	2.262(6)
Ru(1)–C(13)	2.240(6)	Ru(1)–C(14)	2.268(5)
Ru(1)–C(15)	2.310(5)	Ru(2)–C(2)	1.821(4)
Ru(2)–C(3)	2.087(4)	Ru(2)–C(5)	2.083(5)
Ru(2)–C(17)	2.304(5)	Ru(2)–C(18)	2.300(5)
Ru(2)–C(19)	2.245(5)	Ru(2)–C(20)	2.263(6)
Ru(2)–C(21)	2.275(5)	C(1)–O(1)	1.162(6)
C(2)–O(2)	1.158(5)	C(3)–H(3)	1.013(37)
C(3)–C(4)	1.512(6)	C(5)–H(5)	0.937(35)
C(5)–C(6)	1.514(7)	C(11)–C(12)	1.393(9)
C(11)–C(15)	1.424(8)	C(12)–C(13)	1.413(10)
C(13)–C(14)	1.383(12)	C(14)–C(15)	1.442(9)
C(15)–C(16)	1.494(10)	C(16)–H(16a)	0.809(41)
C(16)–H(16b)	0.961(43)	C(16)–C(17)	1.498(8)
C(17)–C(18)	1.422(7)	C(17)–C(21)	1.415(7)
C(18)–C(19)	1.389(8)	C(19)–C(20)	1.426(8)
C(20)–C(21)	1.412(8)		

Ru(2)–Ru(1)–C(1)	108.8(2)	Ru(2)–Ru(1)–C(3)	50.9(1)
C(1)–Ru(1)–C(3)	91.1(2)	Ru(2)–Ru(1)–C(5)	50.8(1)
C(1)–Ru(1)–C(5)	89.5(2)	C(3)–Ru(1)–C(5)	96.6(2)
Ru(1)–Ru(2)–C(2)	108.7(2)	Ru(1)–Ru(2)–C(3)	50.8(1)
C(2)–Ru(2)–C(3)	90.4(2)	Ru(1)–Ru(2)–C(5)	50.8(1)
C(2)–Ru(2)–C(5)	90.0(2)	C(3)–Ru(2)–C(5)	96.5(2)
Ru(1)–C(1)–O(1)	178.6(5)	Ru(2)–C(2)–O(2)	177.9(4)
Ru(1)–C(3)–Ru(2)	78.3(1)	Ru(1)–C(3)–H(3)	112.7(20)
Ru(2)–C(3)–H(3)	110.5(21)	Ru(1)–C(3)–C(4)	124.3(3)
Ru(2)–C(3)–C(4)	124.5(3)	H(3)–C(3)–C(4)	104.9(19)
Ru(1)–C(5)–Ru(2)	78.4(2)	Ru(1)–C(5)–H(5)	111.8(23)
Ru(2)–C(5)–H(5)	114.3(23)	Ru(1)–C(5)–C(6)	125.1(3)
Ru(2)–C(5)–C(6)	124.3(3)	H(5)–C(5)–C(6)	102.4(23)
C(15)–C(16)–C(17)	115.7(5)		

Table 3. Structure analyses

Compound	(1a)	(7)
(a) Crystals data		
Formula	$C_{15}H_{10}O_4Ru_2$	$C_{17}H_{18}O_2Ru_2$
M	456.3	456.5
Crystal system	Orthorhombic	Monoclinic
Space group (no.)	*Pbca*(no. 61)	$P2_1/n$(no. 14)
$a/Å$	18.066(9)	8.702(3)
$b/Å$	14.321(6)	12.653(4)
$c/Å$	22.156(10)	14.508(6)
$\beta/°$	90	98.01(3)
$U/Å^3$	5 732(5)	1 581(1)
T/K	295	295
Z	16	4
$D_c/g\ cm^{-3}$	2.12	1.92
$F(000)$	3 520	896
μ/cm^{-1}	20.8	18.75
(b) Data collection and reduction		
Wavelength/Å	0.710 69	0.710 69
Monochromator	Graphite	Graphite
2θ range/°	4—45	4—55
Scan method	θ—2θ	θ—2θ
Scan width ($2\theta°$)	$2.6 + \Delta_{\alpha1\alpha2}$	$2.4 + \Delta_{\alpha1\alpha2}$
Total data	4 162	2 268
Unique data	3 743	2 029
'Observed' data		
$N_o [F^2 > 2\sigma(F^2)]$	3 009	1 813
Crystal faces	(010)[0.04],(0$\bar{1}$0)[0.04]	(111)[0.15],($\bar{1}\bar{1}\bar{1}$)[0.15]
[distance from	($\bar{1}$01)[0.19],(10$\bar{1}$)[0.19]	(10$\bar{1}$)[0.05],($\bar{1}$01)[0.05]
origin (mm)]	(101)[0.23],($\bar{1}$0$\bar{1}$)[0.23]	(1$\bar{1}$0)[0.16],($\bar{1}$10)[0.16]
Minimum, Maximum transmission coefficients	0.482, 0.847	0.541, 0.838
(c) Refinement		
Least-squares variables, N_v	387	208
R^*	0.045	0.025
R'	0.042	0.026
S	1.99	1.15
g	0.0003	0.0002
Difference map features (e Å^{-3})	+ 0.67, − 1.23	+ 0.39, −0.31

* $R = \Sigma|\Delta|\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma F^2_o)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = |F_o| - |F_c|$ where $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$ and $\sigma_c^2(F_o)$ is the variance in F_o based on counting statistics.

CDCl₃) δ 10.13 (q, *J* 7, 2 H, 2C*H*Me), 5.45, 4.80 (8 H, 2 C₅H₄, [AB]₂ system), 3.36 (s, 2 H, CH₂), and 2.65 (d, *J* 7 Hz, 2 Me); ¹³C-{¹H} n.m.r. (in CDCl₃) δ 23.8 (CH₂), 40.9 (Me), 83.0 (*C*H of C₅H₄), 91.3 (*C*CH₂), 96.4 (*C*H of C₅H₄), 133.4 (μ-C), and 205.1 (CO)].

[Ru₂(CO)₂(μ-CO)(μ-CH₂)(η⁵: η⁵'-C₅H₄CH₂C₅H₄)] (6). To a toluene solution (30 cm³) of complex (1) (0.285 g, 0.62 mmol) was added 3 cm³ of a 1 mol dm⁻³ solution of Li[BHEt₃] in thf. The mixture was stirred for 2 h then water (1 cm³) was added. Solvent was evaporated under reduced pressure and the residue, dissolved in the minimum of dichloromethane, was introduced to an alumina column. Elution with hexane–dichloromethane (3:2) gave a yellow band due to a small amount of (1), while hexane–dichloromethane (2:3) developed a pale yellow band which afforded 87 mg (29%) of yellow-green, powdery (6) [(Found: *M* 443. C₁₅H₁₂O₃Ru₂ requires *M* 443); ν(CO) (in CH₂Cl₂) at 1 981s, 1 944m, and 1 786m cm⁻¹; ¹H n.m.r. (in CDCl₃) δ 9.27 (s, 1 H) and 6.82 (s, 1 H) (μ-CH₂), 5.61 (d, *J* 1.5, 2 H), 5.48 (d, *J* 1.5, 2 H), 5.15 (d, *J* 1.5, 2 H), and 4.99 (d, *J* 1.5 Hz, 2 H) (2C₅H₄), and 3.34 (s, 2 H, CH₂)]. The product could not be completely freed of impurities, despite repeated recrystallisation, and satisfactory analytical data were not obtained.

[Ru₂(CO)₂(μ-CO)(μ-σ: σ'-C₂Ph₂)(η⁵: η⁵'-C₅H₄CH₂C₅H₄)] (5). A mixture of complex (1) (0.2 g, 0.44 mmol) and diphenylacetylene (0.31 g, 1.76 mmol) in toluene (100 cm³) was subjected to u.v. irradiation for 2 h in a silica glass tube while purging with nitrogen. The solvent was then removed at reduced pressure and the residue chromatographed on alumina. Elution with dichloromethane–hexane (2:3) removed a trace of (1), then dichloromethane–hexane (3:2) developed a yellow band which yielded 60 mg (22%) of yellow crystalline (5) as a 0.5 CH₂Cl₂ solvate on recrystallisation from dichloromethane–

hexane [m.p. 156—160 °C (decomp.) (Found: C, 52.7; H, 3.3%; *M* 429 (*M* − PhC₂Ph). C₂₈H₂₀O₃Ru₂·0.5 CH₂Cl₂ requires C, 52.7; H, 3.3%; *M* 608); ν(CO) (in CH₂Cl₂) at 1 989s, 1 960m, and 1 772m cm⁻¹; ¹H n.m.r. (in CDCl₃) δ 7.09 (m, 10 H, 2 Ph), 6.01 (m, 2 H), 5.19 (m, 2 H), 5.09 (m, 2 H), 4.77 (m, 2 H) (2C₅H₄), 3.82 and 3.80 (AB q, 2 H, CH₂); ¹³C-{¹H} n.m.r. (in CDCl₃) δ 25.9 (CH₂), 85.9, 89.1, 89.8, and 91.4 (CH of C₅H₄), 100.3 (*C*CH₂), 115.1 (*C*Ph), 124.4, 127.8, 128.3, and 147.9 (Ph), 201.2 (CO), and 237.1 (μ-CO)].

[Ru₂I₂(CO)₄(η⁵: η⁵'-C₅H₄CH₂C₅H₄)] (2). A mixture of complex (1) (0.1 g, 0.22 mmol) and iodine (200 mg, 0.79 mmol) in chloroform (100 cm³) was stirred at room temperature for 5 min, then the solvent was evaporated under reduced pressure and the residue chromatographed on alumina. Elution with hexane–dichloromethane (3:2) developed a single yellow band which provided 0.14 g, (92%) of yellow-orange crystalline (2) after recrystallisation from hexane–dichloromethane [m.p. 135 °C (Found: C, 26.0; H, 1.5%; *M* 599 (*M* − 4CO). C₁₅H₁₀I₂O₄Ru₂ requires C, 25.4; H, 1.4%; *M* 711; ν(CO) (in

Table 4. Atomic co-ordinates (× 10⁴) for complex (1a)

Atom	x	y	z	Atom	x	y	z
Ru(1)	609(1)	1 792(1)	53(1)	C(10)	1 627(5)	4 872(6)	−111(4)
Ru(2)	839(1)	3 702(1)	58(1)	C(11)	1 775(4)	4 498(6)	463(4)
Ru(3)	3 189(1)	3 584(1)	2 242(1)	C(12)	2 009(4)	3 570(6)	397(4)
Ru(4)	3 127(1)	1 714(1)	2 546(1)	C(13)	2 017(4)	3 372(6)	−235(4)
C(1)	691(4)	1 872(6)	888(4)	C(14)	2 253(4)	2 457(7)	−504(4)
O(1)	769(4)	1 893(5)	1 398(3)	C(15)	1 665(4)	1 713(5)	−498(4)
C(2)	−403(5)	1 998(6)	85(3)	C(16)	1 639(4)	936(6)	−105(4)
O(2)	−1 030(3)	2 108(5)	111(3)	C(17)	1 014(4)	392(6)	−244(4)
C(3)	179(5)	3 869(6)	685(4)	C(18)	665(4)	800(7)	−731(4)
O(3)	−230(4)	4 001(5)	1 068(3)	C(19)	1 051(4)	1 626(6)	−885(4)
C(4)	90(5)	3 766(6)	−504(4)	C(20)	4 032(4)	1 952(6)	3 231(4)
O(4)	−372(4)	3 837(5)	−861(3)	C(21)	3 663(5)	1 120(7)	3 384(4)
C(5)	2 929(5)	3 854(6)	3 035(5)	C(22)	3 750(5)	490(7)	2 918(4)
O(5)	2 788(4)	4 076(5)	3 514(3)	C(23)	4 179(5)	890(7)	2 472(4)
C(6)	2 209(5)	3 629(6)	2 030(4)	C(24)	4 356(4)	1 824(7)	2 659(4)
O(6)	1 578(4)	3 672(5)	1 905(3)	C(25)	4 827(5)	2 525(9)	2 327(5)
C(7)	2 801(4)	1 553(6)	1 763(4)	C(26)	4 398(4)	3 316(7)	2 046(4)
O(7)	2 612(4)	1 428(5)	1 275(3)	C(27)	4 321(6)	4 211(8)	2 282(5)
C(8)	2 157(5)	1 751(7)	2 787(4)	C(28)	3 889(6)	4 739(7)	1 891(7)
O(8)	1 551(3)	1 711(6)	2 957(3)	C(29)	3 705(5)	4 181(9)	1 406(5)
C(9)	1 784(4)	4 162(6)	−540(4)	C(30)	4 008(4)	3 292(7)	1 502(4)

Table 5. Atomic co-ordinates (× 10⁴) for complex (7)

Atom	x	y	z
Ru(1)	1 489(1)	1 932(1)	2 189(1)
Ru(2)	−539(1)	1 363(1)	3 285(1)
C(1)	3 114(6)	2 598(4)	2 889(4)
O(1)	4 165(4)	3 020(3)	3 319(3)
C(2)	196(6)	1 754(4)	4 472(3)
O(2)	622(5)	1 991(3)	5 236(2)
C(3)	1 601(5)	688(3)	3 136(3)
C(4)	2 910(6)	526(4)	3 925(3)
C(5)	−47(5)	2 864(4)	2 815(3)
C(6)	411(6)	3 799(4)	3 446(4)
C(11)	1 277(6)	723(4)	1 002(3)
C(12)	2 465(8)	1 430(5)	891(4)
C(13)	1 787(10)	2 441(5)	746(4)
C(14)	208(10)	2 349(5)	766(3)
C(15)	−167(6)	1 265(5)	942(3)
C(16)	−1 725(9)	811(8)	1 028(4)
C(17)	−2 100(5)	715(4)	2 000(3)
C(18)	−2 984(5)	1 455(4)	2 450(4)
C(19)	−3 074(6)	1 103(5)	3 348(4)
C(20)	−2 316(6)	103(5)	3 473(4)
C(21)	−1 716(6)	−119(4)	2 639(4)

CH_2Cl_2) at 2 049s and 2 000s cm⁻¹; ¹H n.m.r. (in $CDCl_3$) δ 5.45 (m, 4 H), and 5.34 (m, 4 H)(2C_5H_4, [AB]₂ system), and 3.80 (s, 2 H, CH_2); ¹³C-{¹H} n.m.r. (in $CDCl_3$) δ 28.1 (CH_2), 84.4 and 87.8 (CH of C_5H_4), 109.1 (CCH_2), and 195.1 (CO)].

[$Ru_2Me_2(CO)_4$(η⁵: η⁵'-$C_5H_4CH_2C_5H_4$)] (3). A solution of Li[CuMe₂] was prepared by adding methyl-lithium (1 mol dm⁻³ solution in diethyl ether) dropwise, with stirring, to CuI (0.14 g, 0.74 mmol) suspended in thf (5 cm³) until the yellow precipitate formed initially had dissolved. This was then added to a thf solution (30 cm³) of complex (2) (154 mg, 0.22 mmol) and the mixture was stirred at room temperature for 15 min. The solvent was evaporated at reduced pressure and the residue chromatographed on a short alumina column with dichloromethane. No bands were visible but evaporation of the eluent gave 83 mg (79%) of colourless crystalline (3) [(Found: C, 41.5; H, 3.3%; M 487. $C_{17}H_{16}O_4Ru_2$ requires C, 42.0; H, 3.3%; M 487); v(CO) (in CH_2Cl_2) at 2 014s and 1 950s cm⁻¹; ¹H n.m.r. (in

$CDCl_3$) δ 5.17 (m, 4 H) and 5.08 (m, 4 H) (2C_5H_4, [AB]₂ system), 3.13 (s, 2 H, CH_2) and 0.30 (s, 6 H, 2Me)].

Thermolysis of Complex (7).—A solid sample of complex (7) (*ca.* 50 mg) was sealed in an evacuated Pyrex tube (capacity *ca.* 5 cm³) and heated in an oven at 230 °C for 20 h. The evolved gases were then analysed by g.l.c. and identified, by comparison of their retention times with those of authentic samples, as methane (23), ethylene (5), ethane (24), propene (12), but-1-ene (18), *trans*-but-2-ene (12), and *cis*-but-2-ene (6%).

Structure Determinations for Complexes (1a) *and* (7).—Many of the details of the structure analyses carried out are listed in Table 3. X-Ray diffraction measurements were made using Nicolet four-circle $P3m$ diffractometers on single crystals mounted in thin-walled glass capillaries. Cell dimensions for each analysis were determined from the setting angle values of 25 and 14 centred reflections respectively.

Intensity data were collected by θ—2θ scans for unique portions of reciprocal space and corrected for Lorentz, polarisation, crystal decay (of 0 and 2% respectively), and absorption effects, the latter on the basis of the dimensions and the indexed crystal faces of the crystal. Only those reflections with pre-scan counts above a low threshold of 15 counts s⁻¹ were measured for 2θ > 45° for complex (7). The structures were solved by heavy-atom (Patterson and difference Fourier) methods.

The structures were refined by blocked-cascade least squares against F. All non-hydrogen atoms were assigned anisotropic displacement parameters. Methylene and methyne group hydrogen atoms were refined without positional constraints, but with fixed isotropic displacement parameters for (7); for complex (1a), H(14a) and H(14b) were refined without constraints, while H(25a) and H(25b) were constrained to idealised geometry and fixed U_{iso}. All other hydrogen atoms were assigned fixed isotropic displacement parameters and were constrained to ideal geometries with C–H 0.96 Å.

Final difference syntheses showed no chemically significant features, the largest being close to the metal atoms. Refinements converged smoothly to residuals given in Table 3. Tables 4 and 5 report the positional parameters for these structure determinations. All calculations were made with programs of the

SHELXTL[26] system as implemented on a Nicolet R3m/E structure determination system. Complex neutral-atom scattering factors were taken from ref. 27.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

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