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Carbene formation from $CpM(SnPh_3)(CO)_2$ (M = Fe, Ru). Crystal structures of $CpFeI(CO)\{=C(OEt)Ph\}$, $CpRuI(CO)\{=C(OEt)Ph\}$ and $CpRuI(CO)\{=C(NHMe)Ph\}$ *

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Abstract

Addition of LiPh followed by $[Et_3O][BF_4]$ to $CpM(SnPh_3)(CO)_2$ (M = Fe, Ru) gives the carbene complexes $CpM(SnPh_3)(CO)\{=C(OEt)Ph\}$. These undergo aminolysis on treatment with $EtNH_2$ or $MeNH_2$ to form the amino carbenes $CpFe(SnPh_3)(CO)\{=C(NHEt)Ph\}$ and $CpRu(SnPh_3)(CO)\{=C(NHMe)Ph\}$, respectively. All four compounds react with iodine, the $SnPh_3$ group being replaced by I to give the new carbenes $CpMI(CO)\{=C(X)Ph\}$ (M = Fe, Ru; X = OEt; M = Fe, X = NHEt; M = Ru, X = NHMe). The IR and NMR spectra show that the amino carbenes exist as single isomers while the ethoxy carbenes form fluxional isomeric mixtures. The compounds $CpFeI(CO)\{=C(OEt)Ph\}$, $CpRuI(CO)\{=C(OEt)Ph\}$ and $CpRuI(CO)\{=C(NHMe)Ph\}$ have been studied by X-ray diffraction. In each case the geometry about the metal is essentially conventional, with the carbene groups eclipsed by the MCO groups.

Introduction

The reactions of aryl lithium reagents with metal carbonyl complexes followed by alkylation is the basis of the classic Fischer carbene syntheses [1,2]. In particular, it is known that the consecutive reactions of LiPh and $[Et_3O][BF_4]$ with $LM(SnPh_3)(CO)_3$ (M = Mo, W; L = Cp, η^5-C_5Me_5, η^5-indenyl) leads to the "Fischer carbenes" $LM(SnPh_3)(CO)_2\{=C(OEt)Ph\}$ [3,4]. These compounds react with I_2 to form the corresponding iodometal carbene complexes $LMI(CO)_2\{=C(OEt)Ph\}$ [3]. These are useful synthons in connection with our work on migratory reactions to carbenes [5]. We report here the syntheses and characterizations of the correspond-

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* Dedicated to Prof. F.G.A. Stone on the occasion of his 65th birthday.

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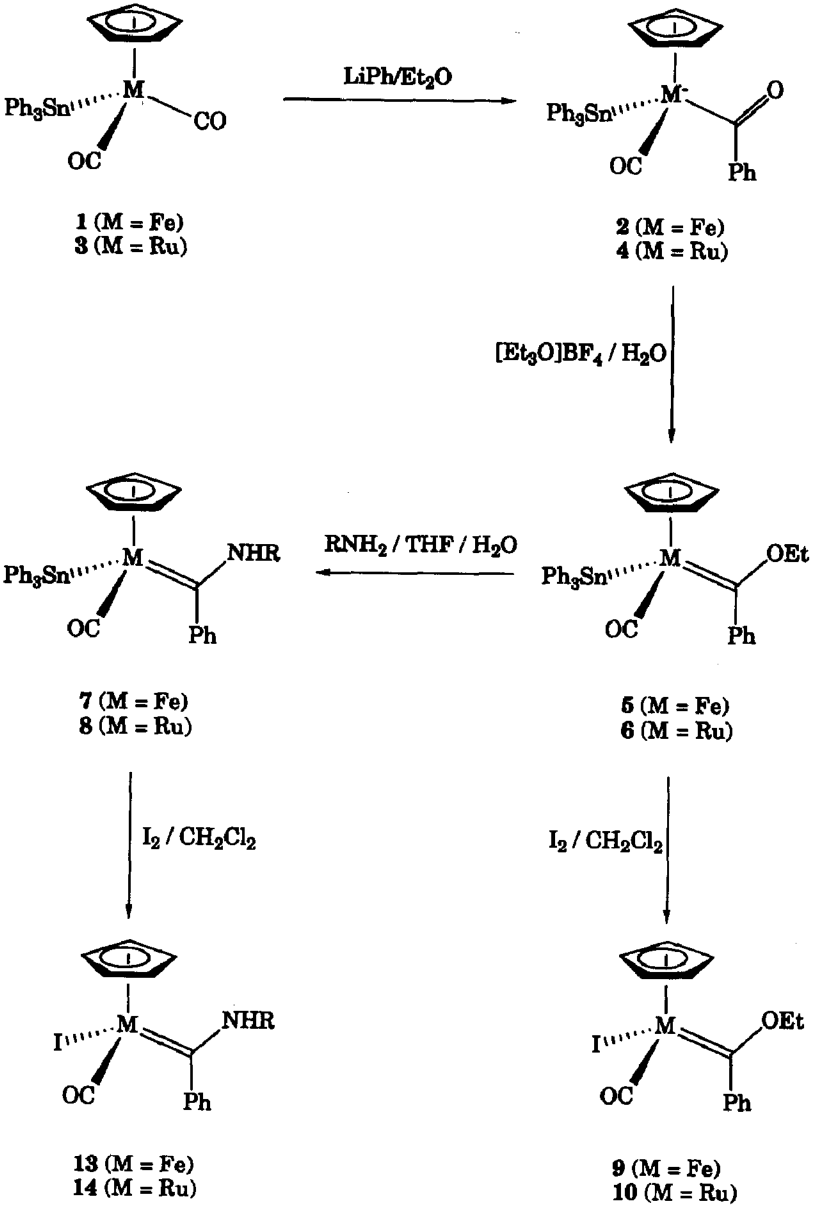
ing Group 8 species $CpM(SnPh_3)(CO)\{=C(OEt)Ph\}$ and $CpMI(CO)\{=C(OEt)Ph\}$ (M = Fe, Ru).

Results and discussion

Preparation of $M(SnPh)_3(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ *(5; M = Fe), (6; M = Ru)*

Addition of LiPh to $Fe(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)$ (**1**) in Et_2O caused a colour change from pale yellow to green over one hour. The IR spectrum [$\nu_{CO}(Et_2O)$, 1897 and 1833 cm^{-1}] contained two bands at lower frequency than those of **1** [$\nu_{CO}(Et_2O)$,



Scheme 1

Table 1

Infrared spectroscopic and physical data for the new compounds

Complex	M.p. (°C)	ν_{CO} (cm^{-1}) [a]	M [b]	Elemental analysis (%) [c]		
				C	H	N
5	130	1929s, 1913m	634, $[M+1]^+$	62.8 (62.6)	4.7 (4.7)	
6	122	1941m, 1925s	678, $[M]^+$	58.7 (58.4)	4.5 (4.4)	
7	125	1897	[d] 633, $[M+1]$	62.5 (62.7)	4.9 (4.9)	2.1 (2.2)
8	132	1910	663, $[M]^+$	57.9 (57.9)	4.4 (4.4)	2.2 (2.1)
9	55 (dec.)	[e] 1993s, 1985m, 1969s	410, $[M]^+$	44.1 (43.9)	3.7 (3.7)	
10	66	[e] 1993w, 1989w, 1969s	456, $[M+1]^+$	39.7 (39.6)	3.7 (3.3)	
11	140	2009s, 1953s, 1721s	458, $[M-2H]^+$	[f]		
13	40	1945	[d] 381, $[M-CO]^+$	[g]		
14	132	1937	441, $[M+1]^+$	38.1 (38.2)	3.1 (3.2)	3.1 (3.2)

[a] Recorded in THF unless stated otherwise. [b] Recorded under electron impact condition unless specified otherwise, [highest observed ion]$^+$. [c] Calculated values in parentheses. [d] Positive ion fab. [e] Recorded in light petroleum solvent. [f] Insufficient material obtained. [g] Adequate analysis not obtained owing to air sensitivity.

1989 and 1933 cm^{-1}], and these new bands are associated with the anionic acyl complex **2** (Scheme 1). We take the presence of two bands as indicative of either an ion pairing phenomenon [6] or the existence of acyl **2** as two species related by different acyl conformations. We have not yet examined this phenomenon in detail. The corresponding reaction of the ruthenium analogue Ru(SnPh$_3$)(CO)$_2$(η-C$_5$H$_5$) (**3**) with LiPh gave the ruthenium acyl **4**, which also showed two ν_{CO} stretches in its IR spectrum [ν_{CO}(Et$_2$O), 1905 and 1849 cm^{-1}].

Removal of ether followed by treatment of the crude products **2** and **4** with [Et$_3$O][BF$_4$] in water gave the carbene complexes **5** and **6**, respectively. The iron species (**5**) was isolated in 57% yield and the ruthenium carbene **6** in 48% yield, yields somewhat higher than those reported for the related GePh$_3$ complex CpFe(GePh$_3$)(CO){=CMe(OMe)} (3%) [3].

The IR spectra of **5** and **6** in THF each contain two overlapping bands in the carbonyl region (Table 1), despite their monocarbonyl stoichiometry. This indicates that compounds **5** and **6** exist as two isomers in solution. However the ambient temperature ^{1}H NMR spectra of **5** and **6** (Table 2) each show only a single set of signals. In both complexes, the two methylene protons are diastereotopic as a consequence of the metal chirality and appear in the spectra as two well-resolved separate double quartets. The two bands in the IR spectra suggest that the ^{1}H NMR spectra are deceptively simple and that the molecule is fluxional. This conclusion is reinforced by the ^{13}C NMR spectra. In both cases only single sets of signals are to be seen at −50 °C in CDCl$_3$. However the spectra at −90 °C in CD$_2$Cl$_2$ each show two sets of signals (Table 2). In the iron case the ratio of major to minor isomers is approximately 3 : 1 whereas in the ruthenium case the ratio is about 20 : 1. In the case of complex **5**, the carbene and methyl signals are not resolved, either because of coincidences or signal to noise problems. In the case of complex **6**, the low abundance of the second isomer in CD$_2$Cl$_2$ at −90 °C means that only the C$_5$H$_5$ and SnPh-*i* signals unambiguously show as pairs of signals.

Table 2

^{1}H and ^{13}C NMR spectra of the complexes

Complex	^{1}H NMR[a] (δ)	^{13}C NMR[b] (δ)
5	7.75–6.75 (m, 20H, Ph), 4.59 (s, 5H, C_5H_5), 3.60 (d q, J = 7, 10 Hz, 1H, CH_2), 3.30 (d q, J = 7, 10 Hz, 1H, CH_2), 0.91 (t, 3H, J = 7 Hz, Me)	major isomer: 313.8 (Fe=C), 217.2 (CO), 151.2 (=CPh-*i*), 144.5 (SnPh-*i*), 138.0–119.0 (Ph), 83.8 (C_5H_5), 70.2 (CH_2), 13.0 (Me) minor isomer: 219.2 (CO), 157.0 (=CPh-*i*), 144.0 (SnPh-*i*), 138.0–119.0 (Ph), 84.4 (C_5H_5), 73.5 (CH_2)
6	7.65–6.95(m, 20H, Ph), 5.00 (s, 5H, C_5H_5), 3.95 (d q, J = 7, 10 Hz, 1H, CH_2), 3.72 (d q, J = 7, 10 Hz, 1H, CH_2), 1.06 (t, 3H, J = 7 Hz, Me)	296.0 (Fe=C), 205.6 (CO), 155.4 (=CPh-*i*), 144.2 (minor SnPh-*i*), 143.7 (major SnPh-*i*), 136.1–124.1 (Ph), 87.7 (major C_5H_5), 87.2 (minor C_5H_5), 74.4 (CH_2), 12.6 (Me)
7	[c] 7.85–6.70 (m, 20H, Ph), 4.42 (s, 5H, C_5H_5), 2.66 (m, 1H, CH_2), 2.18 (m, 1H, CH_2), 0.50 (t, J = 7 Hz, 3H, Me)	[d] 267.8 (Fe=C), 220.3 (CO), 151.0 (=CPh-*i*), 145.8 (SnPh-*i*), 137.3–120.1 (Ph), 82.8 (C_5H_5), 44.2 (CH_2), 14.0 (Me)
8	[c] 7.70–6.75 (m, 20H, Ph), 4.86 (s, 5H, C_5H_5), 2.12 (d, J = 5 Hz, 3H, Me)	[d]252.9 (Fe=C), 206.7 (CO), 150.0 (=CPh-*i*), 145.4 (SnPh-*i*), 137.4–120.3 (Ph), 86.1 (C_5H_5), 35.8 (Me)
9	7.35 (m, 5H, Ph), 4.70 (s, 5 H, C_5H_5), 4.67 (m, 2H, CH_2) 1.50 (t, J = 7 Hz, 3H, Me)	[d,e] 219.2 (CO), 153.7 (Ph-*i*), 129.4–127.7 (Ph), 86.6 (C_5H_5), 15.0 (Me)
10	7.36 (m, 5H, Ph), 5.15 (s, 5H, C_5H_5), 4.85 (m, 2H, CH_2), 1.58 (t, J = 7 Hz, 3H, Me)	major isomer: 301.6 (Fe=C), 204.3 (CO), 154.7 (Ph-*i*), 131.0–124.1 (Ph), 91.0 (C_5H_5), 77.0 (CH_2), 13.9 (Me) minor isomer: 305.8 (Fe=C), 201.7 (CO), 152.9 (Ph-*i*), 131.0–124.1 (Ph), 87.2 (C_5H_5), 78.8 (CH_2), 14.5 (Me)
11	7.75–7.05 (m, 5H, Ph), 4.88 (s, 10H, C_5H_5), 3.49 (q, J = 7 Hz, 2H, CH_2), 1.18 (t, J = 7 Hz, 3H, Me)	
13	9.60 (broad, 1H, NH), 7.40 (m, 2H, Ph), 7.24 (m, 1H, Ph), 7.00 (m, 2H, Ph), 4.36 (s, 5H, C_5H_5), 3.28 (m, 2H, CH_2), 1.18 (t, J = 7 Hz, 3H, Me)	[d] 260.7 (Fe=C), 221.5 (CO), 148.7 (Ph-*i*), 128.1 (Ph), 126.9 (Ph), 83.4 (C_5H_5), 46.1 (CH_2), 14.7 (Me)
14	9.21 (broad, 1H, NH), 7.40 (m, 1H, Ph), 7.26 (m, 2H, Ph), 6.98 (m, 2H, Ph), 4.81 (s, 5H, C_5H_5) 2.93 (d, J = 5 Hz, 3H, Me)	[d] 249.6 (Ru=C), 204.3 (CO), 148.9 (Ph-*i*), 128.1 (Ph), 127.1 (Ph), 120.9 (Ph), 87.3 (C_5H_5), 37.3 (Me)

[a] Recorded in $CDCl_3$ at ambient temperature. [b] Recorded in CD_2Cl_2 solvent at −90 °C unless stated otherwise. [c] No (NH) resonance observed. [d] Recorded in $CDCl_3$ at −50 °C. [e] CH_2 signal coincident with solvent signals.

Related features are apparent in the IR and ^{13}C NMR spectra of the corresponding Group 6 complexes $LM(SnPh_3)(CO)_2\{=C(OEt)Ph\}$ (L = Cp, η-C_5Me_5, η^5-indenyl; M = Mo or W). In these cases the presence of extra IR bands is probably a consequence of restricted rotation about the metal–carbene bond, although this is still under investigation. The situation for complexes **5** and **6** is clearly related.

Preparation of $M(SnPh_3)(CO)\{=C(NHR)Ph\}(\eta$-$C_5H_5)$ (7; M = Fe, R = Et), (8; M = Ru, R = Me)

Both compounds **5** and **6** undergo aminolysis reactions [2,3,7]. As examples, treatment of a THF solution of **5** with aqueous $EtNH_2$ gives the aminocarbene complex **7**, which is isolated as a yellow powder in 88% yield. A solution of the ruthenium compound **6** in THF reacts with aqueous $MeNH_2$ to form compound **8** in 96% isolated yield.

The IR spectra of complexes **7** and **8** both show just a single band in the carbonyl region. There is no sign in the NMR spectra of an isomerization phenomenon related to that displayed by compounds **5** and **6**. That is, just a single set of signals is evident in the NMR spectra down to −50 °C. The NH proton signal is not apparent in the ^{1}H NMR spectra, probably as a consequence of proton exchange with water present in the NMR solvent. However, the adjacent CH_2 group of **7** and the adjacent methyl group of **8** both display coupling to the NH proton. Signals at δ ($CDCl_3$, −50 °C) 267.8 and 252.9 in the ^{13}C NMR spectra of **7** and **8**, respectively, indicate the carbene atoms. Characteristically, the shifts of the amino carbenes are to lower frequency than those of the respective alkoxy carbenes (in this case, **5** and **6**) [2,3].

The observation of just a single isomer for both **7** and **8** again contrasts with the situation for the molybdenum and tungsten compounds $CpM(SnPh_3)(CO)_2\{=C(NHEt)Ph\}$ (R = Me, Et; M = Mo, W), which both exist as slowly interconverting conformers.

Preparation of $MI(CO)\{=C(OEt)Ph\}(\eta$-$C_5H_5)$ (9; M = Fe), (10; M = Ru)

Both compounds **5** and **6** react with I_2 in CH_2Cl_2. The reaction is best carried out by mixing solid I_2 with a solution of the respective starting material at −78 °C followed by warming to ambient temperature. The result is cleavage of the M–Sn bond in each case (a process which produces Ph_3SnI) and formation of the carbenes **9** and **10** respectively. The X-ray crystal structures of both are described below.

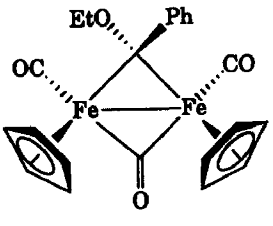
The IR spectrum of **10** in light petroleum shows three carbonyl bands [ν_{CO}(petroleum ether), 1993m, 1989m and 1969s cm^{-1}]. The spectrum is reproducible. This suggests the presence of three isomers. The ^{1}H NMR spectrum of **10** (Table 2) at ambient temperature consists of a singlet for the η-C_5H_5 ligand, a second-order multiplet for the methylene protons, a triplet for the methyl group, and a multiplet for the phenyl group. These signals broaden on cooling to −95 °C in CD_2Cl_2 but we are unable to proceed past this temperature since the solvent freezes. These results suggest a facile fluxional process. The ^{13}C NMR spectrum, however, at −90 °C shows pairs of signals for all the carbon environments within the molecule. The splittings are quite large for the carbene, carbonyl, and Ph-*i* signals, but smaller for the OCH_2 signals. This suggests, but does not prove, that the origin of the splitting is a consequence of restricted rotation about the Ru=C bond, rather than about the O–Et bond. The presence of three IR signals suggests that O–Et rotation does occur, but too quickly to observe at −90 °C in CD_2Cl_2. The presence of three

IR bands rather than four is a consequence either of an accidental coincidence or of a very low population of a fourth isomer in which the Et group clashes with the Cp group. The molybdenum and tungsten compounds $CpMI(CO)_2\{=C(OEt)Ph\}$ (M = Mo, W) clearly display related fluxional processes and here also it is felt that the three observed isomers for each (as seen in the IR spectrum) are associated with restricted rotation about the metal–carbene and carbene–OEt bonds.

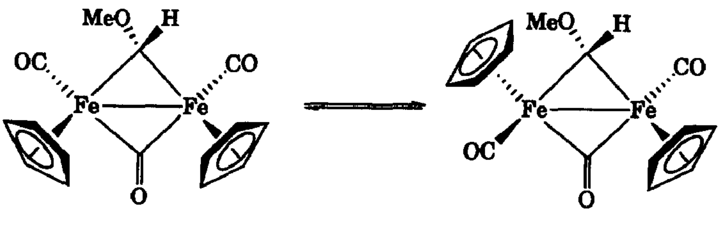
The situation for the iron compound **9** is clearly similar but less clear cut. As for the analogous ruthenium compound **10**, the IR spectrum of **9** in light petroleum contains three carbonyl bands [ν_{CO}(petroleum ether); 1993s, 1985m, and 1969s cm^{-1}]. The ^1H NMR spectrum of **9** is also very similar to that of **10**. In this case there is a partial overlap of the second-order CH_2 multiplet with the Cp signal. Compound **9** is not particularly soluble and consequently the signal to noise ratio in the ^{13}C NMR spectra is poor at −50 °C in $CDCl_3$ and at −90 °C in CD_2Cl_2. It is, however, clear that the molecule is fluxional and we are still making efforts to obtain adequate ^{13}C NMR spectra.

Low temperature chromatography (−50 °C, Al_2O_3) is needed to separate complex **9** from the byproduct, Ph_3SnI. At ambient temperature, compound **9** reacts on Al_2O_3 to give small amounts of a red crystalline material. The ^1H NMR, IR and mass spectra of this decomposition product strongly suggest that it is the bimetallic complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)Ph\}$ (**11**).

The mass spectrum of **11** exhibits a molecular ion at 458 ($[M-2]^+$). The IR spectrum [ν_{CO}(THF), 2009, 1953 and 1721 cm^{-1}] contains a band (1721 cm^{-1}) indicative of a bridging CO, and hence a Fe_2 structure. The ^1H NMR spectrum contains a ten-proton Cp singlet, a quartet for the methylene protons, a triplet for the methyl group, together with multiplets totalling five protons in the phenyl region. The presence of only one Cp signal suggests that the two Cp ligands are mutually *cis*. The related complex **12** [8] exists in solution as a mixture of *cis* and *trans* isomers in the ratio **12t** : **12c** = 1 : 3. The IR spectrum of **12** includes a band at 1776 cm^{-1} as a consequence of the bridging CO.



11



12c **12t**

Preparation of $MI(CO)\{=CPh(NHR)\}(\eta\text{-}C_5H_5)$ (13; M = Fe, R = Et), (14; M = Ru, R = Me)

The reactions of iodine with complexes 7 or 8 results in replacement of the $SnPh_3$ group by I, to give the new carbene complexes 13 and 14, respectively. The X-ray crystal structure of complex 14 is discussed below. The IR spectra of both compounds show just single ν_{CO} stretches and only one set of signals is evident in the ^1H and ^{13}C NMR spectra (at −50 °C in the ^{13}C NMR spectra). Signals assigned to the NH protons are visible as broad signals in the spectra of both compounds, contrasting with the absence of the corresponding signals in the spectra of the starting materials 7 and 8. The existence of 13 and 14 as single isomers contrasts with the behaviour of the related molybdenum and tungsten complexes $CpMI(CO)_2\{=C(NHEt)Ph\}$ (M = Mo, W), which exist in solution as pairs of *cis* isomers. In those cases the isomers are probably related by differing NHEt orientations.

X-ray crystal structures

The molecular structures of CpFeI(CO){=C(OEt)Ph} (9), CpRuI(CO){=C(OEt)Ph} (10), and CpRuI(CO){=C(NHMe)Ph} (14), are illustrated in Figs. 1, 2, and 3 respectively. Details of the structures are presented in Tables 3–9. The structures of all three are closely related. Each consists of the respective metal atom bonded to an iodine, an essentially linear carbonyl, the carbene, and a more or less symmetrically bonded $\eta\text{-}C_5H_5$ ligand. The perpendicular distance of the metal atoms from the mean plane of the Cp rings is shorter for the iron compound (1.750 Å) than in either of the ruthenium cases (for 10, 1.934 Å and for 14, 1.912 Å). The basal ligand angles are all close to 90°. All unconstrained bond

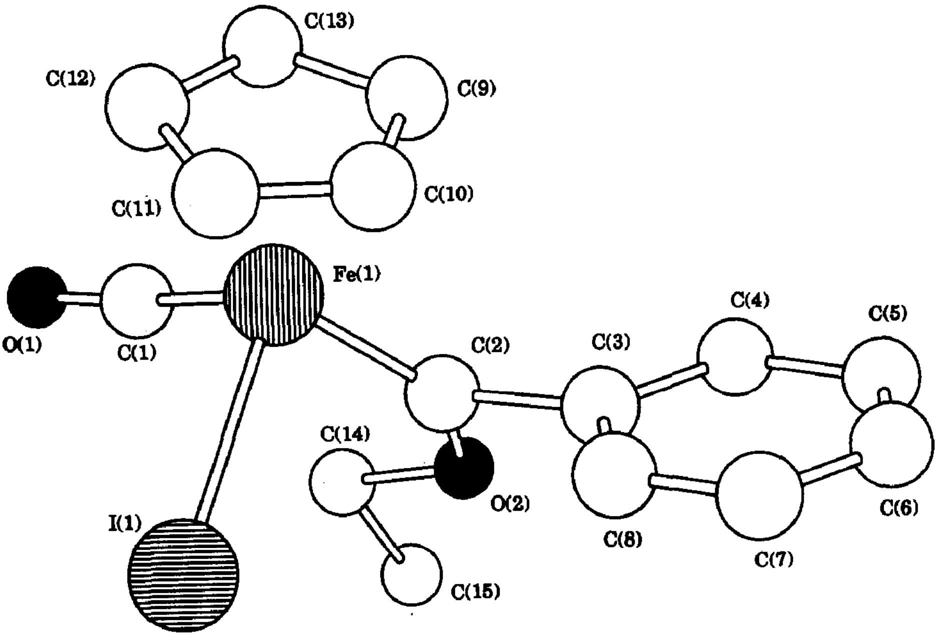


Fig. 1. Molecular structure of CpFeI(CO){=C(OEt)Ph} (9).

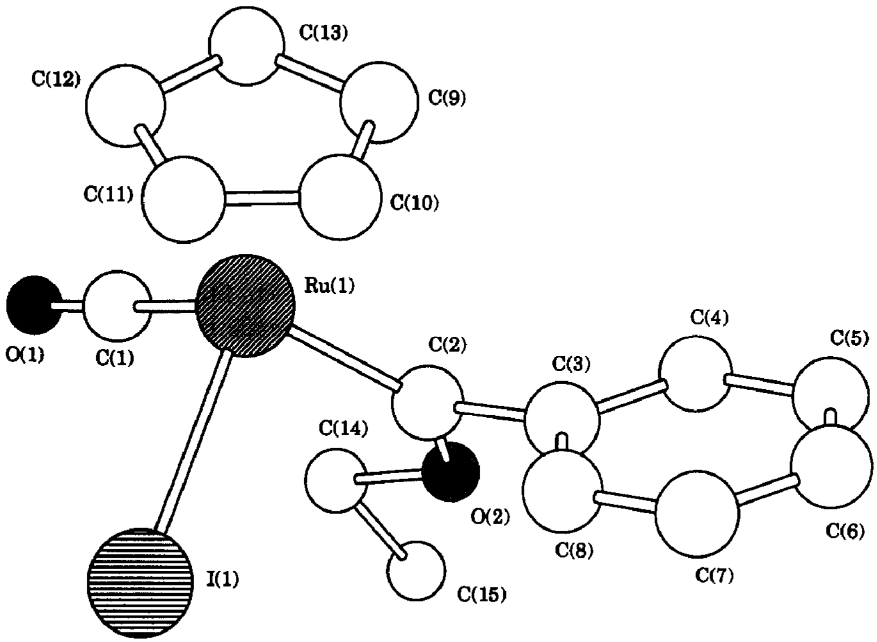


Fig. 2. Molecular structure of CpRuI(CO){=C(OEt)Ph} (**10**).

lengths and angles are unexceptional and there are no significant intermolecular contacts.

The metal to carbene distances are all short (**9**, 1.85 Å; **10**, 2.00 Å; **14**, 2.01 Å). In each of compounds **9** and **10** the =C(OEt)Ph ligand is orientated so that the closely planar phenyl groups are directed towards the cyclopentadienyl ligand. Torsion

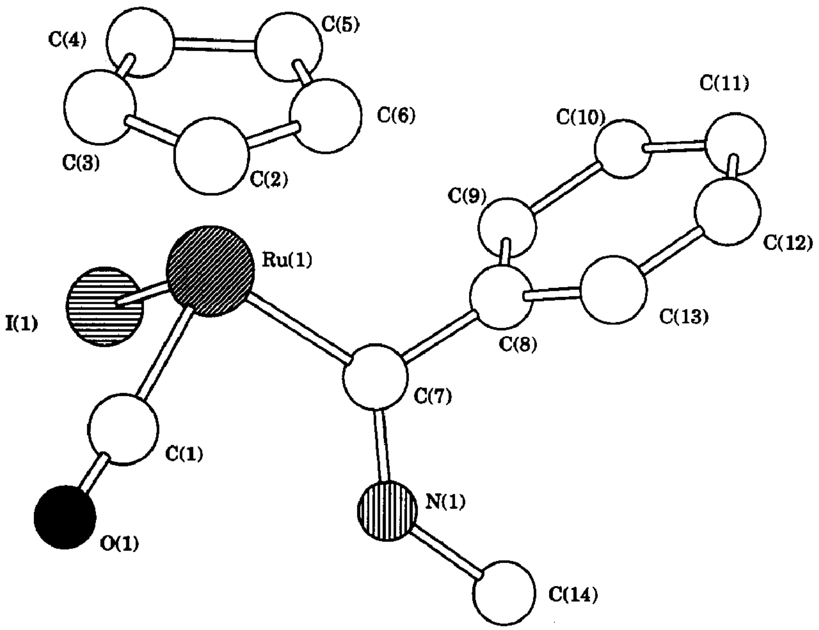


Fig. 3. Molecular structure of CpRuI(CO){=C(NHMe)Ph} (**14**).

angles C(1)–Fe(1)–C(2)–C(3) and I(1)–Fe(1)–C(2)–C(3) are +175 and −96°, respectively, indicating that the plane of the carbene eclipses the more strongly π-accepting ligand. This situation corresponds to that predicted by extended Hückel calculations for asymmetric carbene complexes CpFeL_1L_2(carbene) [9]. A similar effect is seen in other asymmetric complexes of the type CpFeL_1L_2(carbene) [10]. In symmetric complexes of the type CpFeL_2(carbene), the carbene is predicted [11] and observed [12] to adopt a symmetrical structure with the plane of the carbene between the ligands L. Similarly, the torsion angles C(1)–Ru(1)–C(2)–C(3) and I(1)–Ru(1)–C(2)–C(3) are +177 and −93°, respectively. Thus, the π-donor capability of the carbene and the π-acceptor capacity of the carbonyl are linked by common metal *d*-orbitals. The ligand bond angles at C(2) for **9** (104°) and **10** (108°) are small. It is the M(1)–C(2)–O(2) angles which are enlarged in compensation, rather than the angle to the phenyl group. The two aromatic rings are fairly parallel (**9**, 12°; **10**, 14°). However, the coordination plane of the carbene ligands, defined by atoms M(1), O(2), C(2), C(3) is twisted (**9**, 59°; **10**, 60°) from the plane of the cyclopentadienyl ring, and from the phenyl fragments (**9**, 54°; **10**, 53°). This serves to ensure that the rings are laterally displaced, with a shortest contact of 3.25 Å between atoms C(8) and C(10) in **9** and 3.31 Å in **10**.

The structure of complex **14** is related. Here the torsion angles between carbonyl and carbene ligands are C(1)–Ru(1)–C(7)–N(1) +14°, and C(1)–Ru(1)–C(7)–C(8) −168°. Again, the π-donor capability of the carbene and the π-acceptor capacity of the carbonyl are linked by a common metal *d*-orbital.

The phenyl group (r.m.s. deviation 0.012 Å) is again directed towards the η-C_5H_5 ligand, but outwards away from it. The shortest contact is 3.27 Å between atoms C(6) and C(8) and the two aromatic rings are inclined at 26°. The coordination plane of the carbene ligand, defined by atoms Ru(1), N(1), C(7), C(8) (r.m.s. deviation 0.004 Å), is twisted by 64° from the plane of the cyclopentadienyl ring, and by 77° from its own phenyl fragment. In view of the outward directed phenyl ring, the *N*-methyl substituent is obliged to adopt a synperiplanar conformation, with a C(14)–N(1)–C(7)–C(9) torsion angle of −1°: This is in contrast to the structures of **9** and **10** in which antiperiplanar conformations are found. The more nearly mutually perpendicular cyclopentadienyl and carbene planes precludes an antiperiplanar conformation, which would place the *N*-methyl substituent "below" the metal, and in too close proximity. However, as usual, it is not possible to determine whether such conformational differences are intramolecularly directed or due to crystal packing considerations.

Experimental

General procedures

Infrared spectra were recorded on Perkin Elmer 257 or 1710 (Fourier transform, linked to a Perkin Elmer 4600 data station) instruments. Proton NMR spectra were recorded on Bruker WP-80SY (80 MHz), Perkin Elmer R34 (220 MHz), Bruker AM-250 (250 MHz), or Bruker WH-400 (400 MHz) spectrometers. Carbon-13 NMR spectra were recorded on Bruker AM-250 or WH-400 instruments. Mass spectra were recorded with a Kratos MS 25 spectrometer operating at low resolution in the electron impact or fast atom bombardment modes.

All reactions were carried out under dinitrogen or argon with deoxygenated solvents dried with appropriate reagents [THF from Na/benzophenone and light petroleum (b.p. 40–60 ° C throughout) from $LiAlH_4$] or as supplied. Alumina was Brockmann activity II throughout. The compounds $[CpFe(CO)_2]_2$ [13], $[CpRu(CO)_2]_2$ [14], $CpFe(SnPh_3)(CO)_2$ [15], and $CpRu(SnPh_3)(CO)_2$ [16] were synthesized by literature procedures.

Synthesis of $Fe(SnPh_3)(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ (5)

A pale yellow solution of $CpFe(SnPh_3)(CO)_2$ (1) (7.0 g, 13.3 mmol) in Et_2O (100 cm^3) was treated with PhLi (8.6 cm^3, 1.70 M in Et_2O, 16.3 mmol). After 1 h stirring the IR spectrum of the green solution [ν_{CO}(THF), 1897 and 1837 cm^{-1}] indicated the presence of $Li[Fe(SnPh_3)(COPh)(CO)(\eta\text{-}C_5H_5)]$ (2). The solvent was removed under reduced pressure and water (50 cm^3) added. Solid $[Et_3O][BF_4]$ was added in small portions, with stirring, until the mixture gave an alkaline response to pH paper. The crude product was extracted into CH_2Cl_2 (100 cm^3) and the extract filtered through Al_2O_3. The solvent was removed, the product dissolved in hexane/CH_2Cl_2 (3 : 1), the solution was filtered, then reduced in volume and more hexane was added. Cooling to −20 ° C gave the carbene **5** as a yellow powder (4.8 g, 57%).

Synthesis of $Fe(SnPh_3)(CO)\{=C(NHEt)Ph\}(\eta\text{-}C_5H_5)$ (7)

A solution of $Fe(SnPh_3)(CO)\{=CPh(OEt)\}(\eta\text{-}C_5H_5)$ (5) (1.37 g, 2.16 mmol) in THF (50 cm^3) was treated with an excess of $EtNH_2$ (45.0 cm^3, 70% w/v in H_2O). After 2 h stirring the solvent was removed under reduced pressure and a solution of the residue in CH_2Cl_2 filtered through Al_2O_3. Recrystallization from hexane/CH_2Cl_2 gave the carbene **7** as a yellow powder (1.20 g, 88%).

Synthesis of $FeI(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ (9)

A solution of $Fe(SnPh_3)(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ (5) (6.0 g, 9.5 mmol) in CH_2Cl_2 (150 cm^3) was treated with I_2 (2.4 g, 9.5 mmol), at −78 ° C. When warmed to room temperature (ca. 1h) the solution became maroon. The solvent was removed under reduced pressure and the residue chromatographed on Al_2O_3 (15 × 2 cm) at −50 ° C. Elution with light petroleum/CH_2Cl_2 (4 : 1) as eluant gave a red brown band. Recrystallization from light petroleum gave the carbene **9** as maroon needles (2.2 g, 56%).

Synthesis of $FeI(CO)\{=C(NHEt)Ph\}(\eta\text{-}C_5H_5)$ (13)

In a similar procedure to that used in the preparation of **9** above, the reaction of $Fe(SnPh_3)(CO)\{=C(NHEt)Ph\}(\eta\text{-}C_5H_5)$ (7) (4.70 g, 7.4 mmol) with I_2 (1.88 g, 7.4 mmol) gave the carbene **13** as a dark green microcrystalline solid (1.25 g, 41%).

Synthesis of $Ru(SnPh_3)(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ (6)

A colourless solution of $Ru(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)$ (3) (2.4 g, 4.2 mmol) in Et_2O (60 cm^3) was treated with LiPh (5 cm^3, 1.0 *M* in Et_2O, 5 mmol). After 30 min stirring the IR spectrum of the red solution [ν_{CO}(THF), 1905 and 1849 cm^{-1}] indicated the presence of $Li[Ru(SnPh_3)(COPh)(CO)(\eta\text{-}C_5H_5)]$ (4). The solvent was removed under reduced pressure and water (40 cm^3) added. Solid $[Et_3O][BF_4]$ was then added in small portions with stirring until the mixture was mildly acidic. The crude product was extracted twice into CH_2Cl_2 (total 100 cm^3) and the extract filtered through Al_2O_3 (5 × 3 cm). The solvent was removed and a solution of the residue in hexane/CH_2Cl_2 (3 : 1) was filtered and reduced in volume, and more hexane was added. Cooling to −20 °C gave the carbene **6** as pale green/yellow crystals (two crops, 1.33 g, 47%).

Synthesis of $Ru(SnPh_3)(CO)\{=C(NHMe)Ph\}(\eta\text{-}C_5H_5)$ *(8)*

A solution of $Ru(SnPh_3)(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ (**6**) (0.50 g, 0.74 mmol) in THF (10 cm^3) was treated with an excess of $MeNH_2$ (12.5 cm^3, 25/30% w/v in H_2O). After 2 h stirring the solvent was removed under reduced pressure. A solution of the residue in CH_2Cl_2 was filtered through Al_2O_3 (2 × 5 cm) and then evaporated. Recrystallisation of the residue from hexane/CH_2Cl_2 gave the carbene **8** as pale green/yellow crystals (0.47 g, 96%).

Synthesis of $RuI(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ *(10)*

A solution of $Ru(SnPh_3)(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ (**6**) (0.55 g, 0.81 mmol) in CH_2Cl_2 (20 cm^3) was treated with solid I_2 (0.21 g, 0.81 mmol) at −78 °C. As it warmed to room temperature (ca. 1 h) the solution became orange/red. The solvent was removed under reduced pressure and the residue chromatographed on Al_2O_3 (15 × 2 cm) at −50 °C with light petroleum/CH_2Cl_2 (5 : 1) as eluant. Recrystallization of the orange product from light petroleum gave the carbene **10** as bright orange needles (0.27 g, 73%).

Synthesis of $RuI(CO)\{=C(NHMe)Ph\}(\eta\text{-}C_5H_5)$ *(14)*

In a procedure similar to that used in preparation of **10**, $Ru(SnPh_3)(CO)\{=C(NHMe)Ph\}(\eta\text{-}C_5H_5)$ (**8**) (0.44 g, 0.66 mmol) and I_2 (0.17 g, 0.67 mmol) gave the carbene **14** as bright orange/red crystals (0.24 g, 83%), on recrystallization from light petroleum/CH_2Cl_2.

Crystal structures

The X-ray data are summarized in Table 9. For all three structures, the independent data were corrected for Lorentz and polarisation effects, and for absorption by analysis of azimuthal scans. The structures were solved by Patterson and Fourier techniques, and refined by blocked cascade least squares methods. Complex scattering factors were taken from the program package SHELXTL [17] as implemented on the Data General Nova 3 computer.

CpFeI(CO){=C(OEt)Ph} (9). Hydrogen atoms were placed at calculated positions with isotropic thermal parameters related to those of the supporting atom. Allowance was made for the thermal anisotropy of all non-hydrogen atoms. Unit weights were used throughout the refinement. Table 3 lists atomic positional parameters with estimated standard deviations while Table 4 lists bond lengths and bond angles.

CpRuI(CO){=C(OEt)Ph} (10). Geometric constraints were applied to both cyclopentadienyl (D_{5h} symmetry, C–C 1.42 Å) and phenyl (D_{6h} symmetry, C–C 1.395 Å) rings. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final $R = 0.1003$, with allowance for the thermal anisotropy of iodine, ruthenium and oxygen atoms only. Unit weights were used

Table 3

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) with estimated standard deviations for CpFeI(CO){=C(OEt)Ph} (9)

Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	1094(1)	−1334(2)	−155(1)	44(1) *
I(1)	947(1)	2268(1)	306(1)	72(1) *
O(1)	194(3)	−1926(19)	−1328(6)	99(5) *
O(2)	928(2)	−2586(12)	1594(5)	52(3) *
C(1)	548(4)	−1729(20)	−812(8)	65(6) *
C(2)	1185(3)	−2071(14)	1152(7)	37(4) *
C(3)	1627(3)	−2160(17)	2021(7)	47(4) *
C(4)	1752(3)	−3914(18)	2611(8)	54(5) *
C(5)	2148(3)	−3960(20)	3442(8)	62(5) *
C(6)	2407(4)	−2308(25)	3670(8)	76(6) *
C(7)	2283(4)	−576(21)	3100(8)	66(6) *
C(8)	1896(3)	−507(18)	2272(7)	54(4) *
C(9)	1567(4)	−3244(21)	−156(8)	66(6) *
C(10)	1715(4)	−1254(22)	−93(10)	73(6) *
C(11)	1461(5)	−190(23)	−932(11)	87(8) *
C(12)	1156(5)	−1472(22)	−1558(10)	74(7) *
C(13)	1213(4)	−3374(20)	−1091(9)	68(6) *
C(14)	473(3)	−2723(20)	1038(8)	57(5) *
C(15)	302(4)	−3304(27)	1804(10)	94(7) *

* Equivalent isotropic *U* defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 4

Bond lengths (Å) and bond angles (°) for CpFeI(CO){=C(OEt)Ph} (9)

Fe(1)–I(1)	2.620(3)	Fe(1)–C(1)	1.758(13)
Fe(1)–C(2)	1.849(10)	Fe(1)–C(9)	2.090(14)
Fe(1)–C(10)	2.128(16)	Fe(1)–C(11)	2.162(20)
Fe(1)–C(12)	2.128(16)	Fe(1)–C(13)	2.085(15)
O(1)–C(1)	1.157(15)	O(2)–C(2)	1.344(14)
O(2)–C(14)	1.453(11)	C(2)–C(3)	1.532(11)
C(3)–C(4)	1.415(16)	C(3)–C(8)	1.402(16)
C(4)–C(5)	1.406(13)	C(5)–C(6)	1.384(20)
C(6)–C(7)	1.389(20)	C(7)–C(8)	1.387(13)
C(9)–C(10)	1.424(20)	C(9)–C(13)	1.406(14)
C(10)–C(11)	1.371(19)	C(11)–C(12)	1.377(20)
C(12)–C(13)	1.423(20)	C(14)–C(15)	1.508(21)
I(1)–Fe(1)–C(1)	89.8(5)	I(1)–Fe(1)–C(2)	87.6(3)
C(1)–Fe(1)–C(2)	101.7(5)	Fe(1)–C(1)–O(1)	173.3(13)
C(2)–O(2)–C(14)	122.8(7)	O(2)–C(14)–C(15)	106.2(8)
Fe(1)–C(2)–O(2)	133.4(6)	Fe(1)–C(2)–C(3)	122.6(8)
O(2)–C(2)–C(3)	104.0(8)	C(2)–C(3)–C(4)	118.7(9)
C(2)–C(3)–C(8)	121.2(9)	C(4)–C(3)–C(8)	120.0(8)
C(3)–C(4)–C(5)	118.8(11)	C(4)–C(5)–C(6)	119.9(11)
C(5)–C(6)–C(7)	121.4(9)	C(6)–C(7)–C(8)	119.6(12)
C(3)–C(8)–C(7)	120.3(11)	C(10)–C(9)–C(13)	105.7(11)
C(9)–C(10)–C(11)	110.5(11)	C(10)–C(11)–C(12)	107.1(14)
C(11)–C(12)–C(13)	109.5(11)	C(9)–C(13)–C(12)	107.1(11)

Table 5

Atom coordinates $(\times 10^4)$ and temperature factors $(\text{Å}^2 \times 10^3)$ with estimated standard deviations for CpRuI(CO){=C(OEt)Ph} (**10**)

Atom	x	y	z	U_{eq}
I(1)	950(1)	2368(5)	288(3)	103(2) *
Ru(1)	1070(1)	−1318(5)	−172(3)	68(2) *
O(1)	128(12)	−1837(57)	−1304(27)	134(25) *
O(2)	932(8)	−2656(40)	1652(20)	83(15) *
C(1)	473(17)	−1706(80)	−853(40)	106(19)
C(2)	1199(15)	−2177(70)	1234(35)	96(15)
C(3)	1627(6)	−2237(41)	2035(16)	62(11)
C(4)	1752(6)	−3944(41)	2608(16)	107(16)
C(5)	2150(6)	−4053(41)	3428(16)	87(14)
C(6)	2422(6)	−2454(41)	3675(16)	112(17)
C(7)	2296(6)	−747(41)	3102(16)	92(15)
C(8)	1898(6)	−639(41)	2282(16)	72(12)
C(9)	1579(9)	−3341(42)	−218(20)	93(14)
C(10)	1732(9)	−1395(41)	−96(20)	79(12)
C(11)	1464(9)	−316(41)	−966(20)	111(17)
C(12)	1146(9)	−1596(41)	−1627(20)	91(14)
C(13)	1217(9)	−3465(41)	−1164(20)	93(14)
C(14)	465(14)	−2704(75)	1069(34)	104(16)
C(15)	325(15)	−3255(78)	1883(38)	133(20)

* Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

throughout the refinement. Table 5 lists atomic positional parameters with estimated standard deviations while Table 6 lists bond lengths and bond angles. The structure is isomorphous with that of the analogous iron species **9**.

CpRuI(CO){=C(NHMe)Ph} (14). Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final $R = 0.0365$, with allowance for the thermal anisotropy of all non-hydrogen atoms. A weighting

Table 6

Bond lengths (Å) and bond angles (°) for CpRuI(CO){=C(OEt)Ph} (**10**)

I(1)–Ru(1)	2.695(7)	Ru(1)–C(1)	1.913(54)
Ru(1)–C(2)	1.997(52)	Ru(1)–C(9)	2.291(33)
Ru(1)–C(10)	2.285(34)	Ru(1)–C(11)	2.272(37)
Ru(1)–C(12)	2.271(35)	Ru(1)–C(13)	2.282(33)
O(1)–C(1)	1.105(63)	O(2)–C(2)	1.367(69)
O(2)–C(14)	1.485(48)	C(2)–C(3)	1.453(44)
C–C(phenyl)	1.395	C–C(cp)	1.420
C(14)–C(15)	1.526(86)		
I(1)–Ru(1)–C(1)	90.2(17)	I(1)–Ru(1)–C(2)	90.4(14)
C(1)–Ru(1)–C(2)	101.6(24)	C(2)–O(2)–C(14)	123.4(33)
Ru(1)–C(1)–O(1)	174.5(50)	Ru(1)–C(2)–O(2)	130.0(28)
Ru(1)–C(2)–C(3)	122.1(37)	O(2)–C(2)–C(3)	107.8(35)
C(2)–C(3)–C(4)	117.1(23)	C(2)–C(3)–C(8)	122.8(22)
C–C–C(phenyl)	120.0	C–C–C(cp)	108.0
O(2)–C(14)–C(15)	102.1(32)		

Table 7

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for CpRuI(CO){=C(NHMe)Ph} (14)

Atom	*x*	*y*	*z*	U_{eq}
Ru(1)	3445(1)	1723(1)	3434(1)	39(1) *
I(1)	7244(1)	2931(1)	3752(1)	57(1) *
N(1)	2472(9)	4564(5)	3354(5)	47(2) *
O(1)	2448(8)	2804(5)	5867(4)	77(2) *
C(1)	2849(9)	2470(6)	4944(6)	50(2) *
C(2)	1283(13)	−160(7)	3272(8)	87(3) *
C(3)	3081(21)	−535(8)	3593(9)	101(5) *
C(4)	4403(15)	−388(8)	2753(12)	102(5) *
C(5)	3369(21)	83(8)	1814(7)	96(4) *
C(6)	1494(18)	198(7)	2171(9)	95(4) *
C(7)	2749(8)	3363(5)	2775(4)	36(2) *
C(8)	2544(9)	3243(5)	1472(5)	42(2) *
C(9)	4217(11)	3288(7)	817(6)	62(3) *
C(10)	4012(14)	3132(9)	−397(7)	81(3) *
C(11)	2151(16)	2988(8)	−953(7)	92(4) *
C(12)	490(13)	2918(8)	−295(6)	79(3) *
C(13)	697(11)	3085(7)	903(6)	61(3) *
C(14)	2011(12)	5800(6)	2913(6)	67(3) *

* Equivalent isotropic *U* defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 8

Bond lengths (Å) and bond angles (°) for for CpRuI(CO){=C(NHMe)Ph} (14)

Ru(1)–I(1)	2.713(2)	Ru(1)–C(1)	1.860(7)
Ru(1)–C(2)	2.225(8)	Ru(1)–C(3)	2.267(8)
Ru(1)–C(4)	2.280(9)	Ru(1)–C(5)	2.263(8)
Ru(1)–C(6)	2.209(9)	Ru(1)–C(7)	2.009(6)
N(1)–C(14)	1.469(9)	N(1)–C(7)	1.301(7)
O(1)–C(1)	1.119(8)	C(2)–C(3)	1.375(17)
C(2)–C(6)	1.394(14)	C(3)–C(4)	1.363(18)
C(4)–C(5)	1.450(17)	C(5)–C(6)	1.364(18)
C(7)–C(8)	1.500(8)	C(8)–C(9)	1.390(9)
C(8)–C(13)	1.382(9)	C(9)–C(10)	1.393(10)
C(10)–C(11)	1.385(14)	C(11)–C(12)	1.385(13)
C(12)–C(13)	1.376(10)		
I(1)–Ru(1)–C(1)	92.4(2)	I(1)–Ru(1)–C(7)	88.2(2)
C(1)–Ru(1)–C(7)	93.3(3)	C(7)–N(1)–C(14)	129.2(6)
Ru(1)–C(1)–O(1)	174.0(6)	C(3)–C(2)–C(6)	106.2(9)
C(2)–C(3)–C(4)	110.4(10)	C(3)–C(4)–C(5)	107.2(10)
C(4)–C(5)–C(6)	105.4(9)	C(2)–C(6)–C(5)	110.9(10)
Ru(1)–C(7)–N(1)	127.3(4)	Ru(1)–C(7)–C(8)	118.5(4)
N(1)–C(7)–C(8)	114.3(5)	C(7)–C(8)–C(9)	120.3(5)
C(7)–C(8)–C(13)	120.8(5)	C(9)–C(8)–C(13)	118.9(6)
C(8)–C(9)–C(10)	119.9(7)	C(9)–C(10)–C(11)	120.4(8)
C(10)–C(11)–C(12)	119.2(7)	C(11)–C(12)–C(13)	120.2(8)
C(8)–C(13)–C(12)	121.2(7)		

Table 9

Summary of crystal data for CpFeI(CO){=C(OEt)Ph} (**9**), CpRuI(CO)P{=C(OEt)Ph} (**10**), and CpRuI(CO){=C(NHMe)Ph} (**14**)

	9	**10**	**14**
Formula	$C_{15}H_{15}FeIO_2$	$C_{15}H_{15}IO_2Ru$	$C_{14}H_{14}INORu$
Molecular weight	410.03	455.26	440.24
Crystal form (solvent)	red elongated plates (hexane)	orange elongated plates (petroleum ether)	orange/red needles (CH_2Cl_2/petroleum ether)
Crystal size (mm)	$0.35 \times 0.225 \times 0.10$	$0.40 \times 0.225 \times 0.075$	$0.40 \times 0.20 \times 0.125$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$ (C_{2h}^6, No. 15)	$C2/c$ (C_{2h}^6, No. 15)	$P\bar{1}$(C_i^1, No. 2)
a (Å)	34.818(36)	35.22(8)	6.800(4)
b (Å)	6.730(5)	6.854(9)	9.925(9)
c (Å)	14.452(16)	14.660(24)	11.628(10)
α (°)	90.000	90.000	99.92(7)
β (°)	114.39(8)	115.82(14)	91.77(6)
γ (°)	90.000	90.000	96.27(6)
U (Å^3)	3084(5)	3186(9)	767.4(11)
D_c (g cm^{-3})	1.766	1.898	1.905
Z	8	8	2
Radiation (λ, Å)	Mo-K_α (0.71069)	Mo-K_α (0.71069)	Mo-K_α (0.71069)
μ (Mo-K_α) (cm^{-1})	29.53	28.79	29.82
F(000)	1599.82	1743.86	419.96
Diffractometer	Nicolet R3 four circle	Nicolet R3 four circle	Nicolet R3 four circle
Temperature	ambient	ambient	ambient
Scan type	ω	ω	ω
2θ range (°)	3.5–50	3.5–50	3.5–50
Total data	3022	3219	2708
Unique observed	1880 [$\|F\|/\sigma(\|F\|) > 3.0$]	950 [$\|F\|/\sigma(\|F\|) > 4.0$]	2245 [$\|F\|/\sigma(\|F\|) > 3.0$]
R	0.0604	0.1003	0.0365
R_w	–	–	0.0366

scheme $w^{-1} = [\sigma^2(F) + g(F)^2]$ with $g = 0.00030$ was used in that latter stages of refinement. Table 7 lists atomic positional parameters with estimated standard deviations while Table 8 lists bond lengths and bond angles.

Supplementary material available. Tables listing anisotropic temperature factors, and hydrogen atom coordinates and temperature factors for compound **9**, **10**, and **14** are available from the authors.

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References

1 E.O. Fischer and A. Maasbol, Angew. Chem. Int. Ed. Engl., 3 (1964) 580.

2 Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983.

3 W.K. Dean and W.A.G. Graham, Inorg. Chem., 16 (1977) 1061.

4 G.W. Bentley, G. Hough, M.J. Winter and S. Woodward, Polyhedron, 8 (1989) 1861.

5 (a) V.A. Osborn, C.A. Parker, and M.J. Winter, J. Chem. Soc., Chem. Commun., (1986) 1185; (b) M.J. Winter and S. Woodward, J. Organomet. Chem., 361 (1989) C18; (c) M.J. Winter, Polyhedron, 8 (1989) 1583; (d) C.E. Davey, R. Devonshire and M.J. Winter, Polyhedron, 8 (1989) 1863; (e) M.J. Winter and S. Woodward, J. Chem. Soc., Chem. Commun., (1989) 457.

6 M.Y. Darensbourg, Prog. Inorg. Chem., 33 (1985) 221.

7 J.A. Connor and E.O. Fischer, J. Chem. Soc. A, (1969) 578.

8 S.C. Kao, P.P.Y. Lu and R. Pettit, Organometallics, 1 (1982) 911.

9 B.E.R. Schilling, R. Hoffmann and J.W. Faller, J. Am. Chem. Soc., 101 (1979) 592.

10 H. Adams, N.A. Bailey, M. Grayson, C. Ridgway, A.J. Smith, P. Taylor and M.J. Winter, Organometallics, in press.

11 B.E.R. Schilling, R. Hoffmann and D.L. Lichtenberger, J. Am. Chem. Soc., 101 (1979) 585.

12 A.M. Crespi and D.F. Shriver, Organometallics, 4 (1985) 1830; (b) C. Knors, G.-H. Kuo, J.W. Lauher, C. Eigenbrot and P. Helquist, Organometallics, 6 (1987) 988.

13 J.J. Eisch and R.B. King (Eds.), Organometallic Syntheses, Vol. 1, Academic Press, New York and London, 1965.

14 N.M. Doherty and S.A.R. Knox, Inorg. Synth., 25 (1989) 179.

15 R.D. Gorsich, J. Am. Chem. Soc., 84 (1962) 2486.

16 D.H. Gibson, W.L. Hsu and F.U. Ahmed, J. Organomet. Chem., 215 (1981) 379.

17 G.M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data (Revision 4), University of Gottingen, F.R.G., 1983.