ELSEVIER

Journal of Organometallic Chemistry 579 (1999) 75–82

Journal of Organometallic Chemistry

Mixed-metal cluster chemistry XII: isocyanide derivatives of [CpWIr$_3$(CO)$_{11}$]; X-ray crystal structure of [CpWIr$_3$(CO)$_9$(CNC$_6$H$_3$Me$_2$-2,6)$_2$]☆

Susan M. Waterman [a], Mark G. Humphrey [a,]*, David C.R. Hockless [b]

[a] *Department of Chemistry, Australian National University, Canberra, A.C.T. 0200, Australia*
[b] *Research School of Chemistry, Australian National University, Canberra, A.C.T. 0200, Australia*

Received 12 October 1998

Abstract

Reactions of [CpWIr$_3$(CO)$_{11}$] (**1**) with stoichiometric amounts of isocyanides afford the clusters [CpWIr$_3$(CO)$_{11-n}$(CNR)$_n$] [R = Xy (C$_6$H$_3$Me$_2$-2,6), n = 1 (**2**), 2 (**3**), 3 (**4**); R = ^{t}Bu, n = 1 (**5**), 2 (**6**), 3 (**7**)] in good to excellent yields (47–63%). The products exhibit ligand fluxionality in solution, with the ^{13}C-NMR spectra of **4**-**6** revealing that the carbonyls are undergoing fast exchange at 143 K. A single-crystal X-ray study of [CpWIr$_3$(CO)$_9$(CNXy)$_2$] (**3**) reveals that the coordination sphere of the cluster has an all-terminal ligand geometry, the first for a ligand substituted derivative of **1**. The two iridium-ligated 2,6-dimethylphenylisocyanide ligands are coordinated to the same iridium vertex, the second example of this coordination geometry for a transition metal cluster. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten; Iridium carbonyl; Isocyanide; Fluxionality

---

1. Introduction

The ligand substitution chemistry of homometallic clusters has been studied intensively [2,3], but ligand replacement at heterometallic clusters has been the subject of comparatively few reports. Incorporation of a heterometal into a cluster core affords the possibility of not only metalloselectivity upon ligand substitution, but also site selectivity due to a decrease in molecular symmetry. With these ideas in mind, we have been examining the effect of replacing the Ir(CO)$_3$ vertices in the tetrahedral [Ir$_4$(CO)$_{12}$] by isolobal CpM(CO)$_2$ (M = Mo, W) units upon phosphine reactivity, alkyne reactivity, and ligand fluxionality [1,4–10]. The replacement of carbonyl by P-donor ligands in both [Ir$_4$(CO)$_{12}$] [11–24] and the isolobally-related [CpWIr$_3$(CO)$_{11}$] (**1**) [5,6,9] usually results in the carbonyl ligand geometry in the ground state shifting from all-terminal to one in which the three edges of one face of the tetrahedral core are spanned by bridging carbonyls. This affords three different ligation sites with respect to the M$_3$(μ-CO)$_3$ plane, namely radial, axial and apical (Fig. 1), all potentially available for incoming ligands. The X-ray structurally characterized examples are consistent with substitution proceeding in a stepwise fashion at unsubstituted Ir(CO)$_3$ vertices, to afford the coordination geometries shown in Table 1. The sites of substitution in the P-ligand substituted clusters are readily rationalized from a combination of steric and electronic factors [25].

Isocyanide substitution at homometallic clusters has also been of significant interest [34–42]. The cone angles of isocyanides CNR are small for a wide range of R substituents, substantially decreasing the importance of steric requirements in controlling product distribu-

---

☆ For part XI see Ref. [1].

* Corresponding author. Tel.: +61-2-6249-2927; fax: +61-2-6249-0760.

E-mail address: mark.humphrey@anu.edu.au (M.G. Humphrey)

0022-328X/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.

PII: S0022-328X(98)01200-5

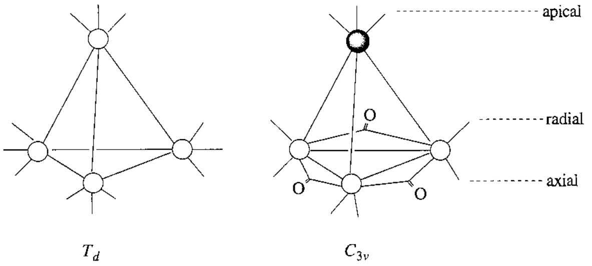


Fig. 1. Carbonyl locations in tetrahedral clusters.

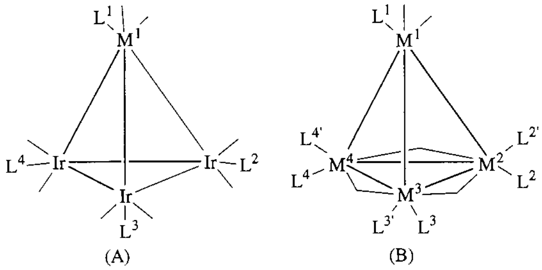
tion. As a result, different coordination geometries from those obtained with phosphines are frequently observed [e.g. phosphine substitution at $[Ru_3(CO)_{12}]$ proceeds to afford sterically-driven equatorially-ligated products (with respect to the Ru_3 plane), whereas isocyanide substitution affords electronically-preferred axially-coordinated derivatives [43]]. Despite comprehensive investigations with homometallic clusters, the reactivity of isocyanides with mixed-metal carbonyl clusters has been comparatively less well studied. We report herein the reactivity of **1** toward one, two or three equivalents of XyNC ($Xy = C_6H_3Me_2$-2,6) or ^{t}BuNC, the characterization by a single-crystal X-ray study of $[CpWIr_3(CO)_9(CNXy)_2]$ (**3**), the thermolyses of the clusters **5**–**7**, and a comparison of our results to those obtained with the $[Ir_4(CO)_{12}]$ system.

2. Results and discussion

2.1. *Syntheses and characterization of* ***2***–***7***

The reactions of $[CpWIr_3(CO)_{11}]$ (**1**) with *n* equivalents of 2,6-dimethylphenylisocyanide (CNXy) or *t*-butylisocyanide ($n = 1$–3) proceed in dichloromethane at room temperature (r.t.) to afford the clusters $[CpWIr_3(CO)_{11-n}(CNXy)_n]$ [$n = 1$ (**2**), 2 (**3**) or 3 (**4**)] or $[CpWIr_3(CO)_{11-n}(CNBu^t)_n]$ [$n = 1$ (**5**), 2 (**6**) or 3 (**7**)], respectively, as the major or sole reaction products in good to excellent yields (Scheme 1). The clusters **2**–**7** have been characterized by a combination of IR, ^{1}H-

Table 1
X-ray crystallographically verified coordination geometries for *P*-ligand derivatives of $[Ir_4(CO)_{12}]$ and $[CpWIr_3(CO)_{11}]$

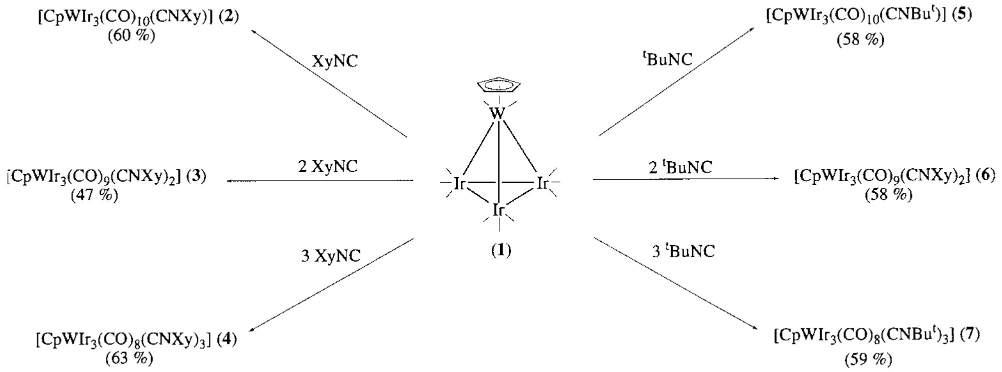


Cluster	Type	Sites of substitution [c]	Ref.
$[Ir_4(CO)_{11}\{\eta^1\text{-}[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)\}]$	A	L^1 ($M^1 = Ir$)	[26]
$[Ir_4(CO)_{11}\{P(OCH_2)_3CEt\}]$	A	L^1 ($M^1 = Ir$)	[27]
$[CpWIr_3(CO)_{11}]$	A	L^1 ($M^1 = W$)	[28,29]
$[Ir_4(\mu\text{-}CO)_3(CO)_7(PPh_3)_2]$	B	$L^{2'}$, L^3 ($M^1 = Ir$)	[14,30]
$[Ir_4(\mu\text{-}CO)_3(\mu\text{-}dmpe)(CO)_7]$	B	L^2, L^3 ($M^1 = Ir$)	[23]
$[Ir_4(\mu\text{-}CO)_3(\mu\text{-}dppb)(CO)_7]$	B	L^2, L^3 ($M^1 = Ir$)	[31]
$[Ir_4(\mu\text{-}CO)_3(\mu\text{-}dppee)(CO)_7]$ [a]	B	L^2, L^3 ($M^1 = Ir$)	[22]
$[CpWIr_3(\mu\text{-}CO)_3(CO)_7(PPh_3)]$	B	$L^{4'}$, L^2 ($M^2 = W$)	[9]
$[CpWIr_3(\mu\text{-}CO)_3(CO)_7(PMe_3)]$	B	L^1, L^2 ($M^1 = W$)	[9]
$[CpWIr_3(\mu\text{-}CO)_3(CO)_7(PMe_2Ph)]$	B	L^1, L^2 ($M^1 = W$)	[5]
$[Ir_4(\mu\text{-}CO)_3(CO)_6(PPh_2pyl)_3]$ [b]	B	$L^{2'}$, $L^{3'}$, L^4 ($M^1 = Ir$)	[32]
$[CpWIr_3(\mu\text{-}CO)_3(CO)_6(PPh_3)_2]$	B	$L^{2'}$, L^3, L^4 ($M^3 = W$)	[9]
$[CpWIr_3(\mu\text{-}CO)_3(CO)_6\{P(Oph)_3\}_2]$	B	$L^{2'}$, L^3, L^4 ($M^3 = W$)	[6]
$[CpWIr_3(\mu\text{-}CO)_3(\mu\text{-}dppm)(CO)_6]$	B	L^1, L^2, L^3 ($M^1 = W$)	[10]
$[CpWIr_3(\mu\text{-}CO)_3(\mu\text{-}dppe)(CO)_6]$	B	L^1, L^2, L^3 ($M^1 = W$)	[10]
$[CpWIr_3(\mu\text{-}CO)_3(\mu\text{-}dppa)(CO)_6]$	B	L^1, L^2, L^4 ($M^1 = W$)	[10]
$[Ir_4\{\mu_3\text{-}HC(PPh_2)_3\}(CO)_9]$	A	L^1, L^2, L^3 ($M^1 = Ir$)	[20]
$[Ir_4(\mu\text{-}CO)_3(CO)_5(PMe_3)_4]$	B	L', L^2, L^3, L^4 ($M^1 = Ir$)	[16,33]
$[Ir_4(\mu\text{-}CO)_3(CO)_5(PMe_2Ph)_4]$	B	L^1, L^2, L^3, L^4 ($M^1 = Ir$)	[19]
$[Ir_4(\mu\text{-}CO)_3(\mu\text{-}dppm)_2(CO)_5]$	B	L^1, $L^{2'}$, L^3, L^4 ($M^1 = Ir$)	[21]

[a] dppee, 1,2-*cis*-Bis(diphenylphosphino)ethene.

[b] PPh_2pyl, diphenyl-2-pyridylphosphine.

[c] Unless otherwise indicated M≡Ir.



Scheme 1. Reactions of $[CpWIr_3(CO)_{11}]$ (**1**) with RNC ($R = C_6H_3Me_2$-2,6, ^{t}Bu). Reaction conditions: CH_2Cl_2, r.t., 16 h.

and ^{13}C-NMR (for **5**–**7**) spectroscopies, mass spectrometry and, in the case of **2**, **3**, **5** and **6**, satisfactory microanalyses (the tris-substituted derivatives **4** and **7** proved unstable in solution over a period of time, precluding successful recrystallization. We have previously noted a similar instability with $[CpWIr_3(\mu\text{-}CO)_3(CO)_5(PMe_3)_3]$ [9] and $[CpWIr_3(\mu\text{-}CO)_3(CO)_5\{P(OPh)_3\}_3]$ [6]). IR spectra suggest the presence of edge-bridging carbonyl ligands in the more highly substituted clusters **3**, **4**, **6** and **7** [ν(CO) 1847–1816 cm^{-1}]. In combination with the X-ray structural results detailed below, the number of bands in the terminal carbonyl ligand ν(CO) regions of the IR spectra of **3**, **4**, **6** and **7** are indicative of the presence of isomers. Complexes **2** and **5** have IR absorptions consistent with the presence of terminal carbonyls only, suggesting a ligand disposition similar to the precursor **1**. The ^{1}H-NMR spectra contain signals assigned to cyclopentadienyl, phenyl and methyl groups for **2-4** and cyclopentadienyl and methyl groups for **5-7**, in the appropriate ratios. The mass spectra of complexes **2-7** contain molecular ions, and all spectra contain fragment ions corresponding to stepwise loss of carbonyls; in all cases, the base peak is $[M-3CO]^+$. Isotope patterns are consistent with the presence of three iridium atoms and one tungsten atom.

2.2. X-ray structural study of 3

The molecular structure of **3** as determined by a single-crystal X-ray study is consistent with the formulation given above and defines the substitution sites of the isocyanides. A summary of crystal and refinement data is found in Table 2, and selected bond distances and angles are listed in Table 3. An ORTEP plot showing the molecular geometry and atomic numbering scheme is shown in Fig. 2.

Complex **3** has the WIr_3 pseudotetrahedral framework of the precursor cluster **1** and possesses an η^5-cyclopentadienyl group, nine terminal carbonyl ligands, and two iridium-ligated 2,6-dimethylphenylisocyanide ligands. The WIr_3 core distances [W–Ir 2.781(1), 2.8282(9), 2.8502(1); Ir–Ir 2.682(1), 2.695(1), 2.7229(8) Å] are similar to those of **1** [W–Ir 2.7920(10), 2.8151(10), 2.8648(10); Ir–Ir 2.6967(9), 2.6985(10), 2.7018(9) Å]. The longest W–Ir distance for **3** is effectively *trans* to the Cp group. Ir–CO(terminal) [1.88(2)–1.94(2) Å] and W–CO interactions [1.96(1), 1.98(2) Å] for **3** are unexceptional. The Ir–CN [1.96(2), 2.01(1)], IrC–N [1.13(2), 1.14(2)] and N–C(aryl) [1.39(2), 1.40(2) Å] distances and Ir–C–N [174(1), 176(1)°] and C–N–C(aryl) [174(2), 168(2)°] angles are consistent with the expected valence bond structure Ir–C≡N–Xy. The Ir–CN linkages are (on average) longer than the Ir–CO distances, consistent with the enhanced Ir→CO π* backbonding of the carbonyl ligand. Ir(1) is in a unique environment, being linked to one terminal carbonyl ligand and two terminal 2,6-dimethylphenylisocyanide ligands. The isocyanide ligands are *trans* to Ir–Ir linkages, and the unique carbonyl ligand at Ir(1) is *trans* to the W–Ir linkage. This site selection may be determined

Table 2
Crystallographic data for **3**

Empirical formula	$C_{32}H_{23}Ir_3N_2O_9W$
Formula weight	1340.05
Space group	$P2_1/n$ (No.14)
Crystal system	Monoclinic
Unit cell dimensions	
a (Å)	14.339(4)
b (Å)	12.772(4)
c (Å)	18.399(5)
β (°)	96.62(2)
V (Å^3)	3347(2)
$D_{calc.}$ (g cm^{-3})	2.659
Z	4
μ (mm^{-1})	15.4
Specimen size (mm^3)	0.48 × 0.37 × 0.24
A (min., max.)	0.45, 1.00
$2\theta_{max}$ (°)	50.1
N	6224
N_o	3832
R	0.040
R_w	0.031

Table 3
Selected bond lengths (Å) and bond angles (°) for complex **3**

Bond lengths (Å)			
Ir(1)–Ir(2)	2.7229(8)	Ir(1)–Ir(3)	2.682(1)
Ir(2)–Ir(3)	2.695(1)	Ir(1)–W(1)	2.8502(8)
Ir(2)–W(1)	2.8282(9)	Ir(3)–W(1)	2.781(1)
Ir(1)–C(11)	1.86(2)	Ir(1)–C(12)	1.96(2)
Ir(1)–C(13)	2.01(1)	Ir(2)–C(21)	1.88(2)
Ir(2)–C(22)	1.90(2)	Ir(2)–C(23)	1.94(2)
Ir(3)–C(31)	1.89(2)	Ir(3)–C(32)	1.91(2)
Ir(3)–C(33)	1.95(2)	W(1)–C(01)	2.36(2)
W(1)–C(02)	2.26(2)	W(1)–C(03)	2.31(2)
W(1)–C(04)	2.36(2)	W(1)–C(05)	2.35(2)
W(1)–C(06)	1.98(2)	W(1)–C(07)	1.94(1)
Bond angles (°)			
Ir(2)–Ir(1)–Ir(3)	59.81(2)	Ir(2)–Ir(1)–W(1)	60.94(2)
Ir(3)–Ir(1)–W(1)	60.27(3)	Ir(1)–Ir(2)–Ir(3)	59.35(2)
Ir(1)–Ir(2)–W(1)	61.75(2)	Ir(3)–Ir(2)–W(1)	60.42(3)
Ir(1)–Ir(3)–Ir(2)	60.84(2)	Ir(1)–Ir(3)–W(1)	62.86(3)
Ir(2)–Ir(3)–W(1)	62.16(3)	Ir(1)–W(1)–Ir(2)	57.31(2)
Ir(1)–W(1)–Ir(3)	56.87(2)	Ir(2)–W(1)–Ir(3)	57.42(2)
Ir(2)–Ir(1)–C(11)	89.6(5)	Ir(3)–Ir(1)–C(11)	97.3(4)
W(1)–Ir(1)–C(11)	148.8(4)	Ir(2)–Ir(1)–C(12)	155.4(4)
Ir(2)–Ir(1)–C(13)	105.2(4)	Ir(3)–Ir(1)–C(12)	95.6(4)
Ir(3)–Ir(1)–C(13)	158.2(4)	W(1)–Ir(1)–C(12)	109.4(4)
W(1)–Ir(1)–C(13)	99.2(4)	C(11)–Ir(1)–C(12)	93.2(6)
C(11)–Ir(1)–C(13)	93.8(6)	C(12)–Ir(1)–C(13)	98.5(6)
Ir(1)–C(11)–O(11)	177(1)	Ir(1)–C(12)–N(12)	174(1)
Ir(1)–C(13)–N(13)	176(1)		

by the nature of the *trans*-disposed ligand; the isocyanides are *trans* to CO groups, and the CO ligand is *trans* to the Cp ligand, both of which should maximize back-bonding to the carbonyls, and are consistent with the site selection being driven by electronic considerations. It is perhaps surprising that both isocyanides ligate the same iridium. Although steric considerations may disfavor coordination at the site occupied by CO(21) and CO(31), it is not clear why coordination at CO(22) and CO(33) does not proceed.

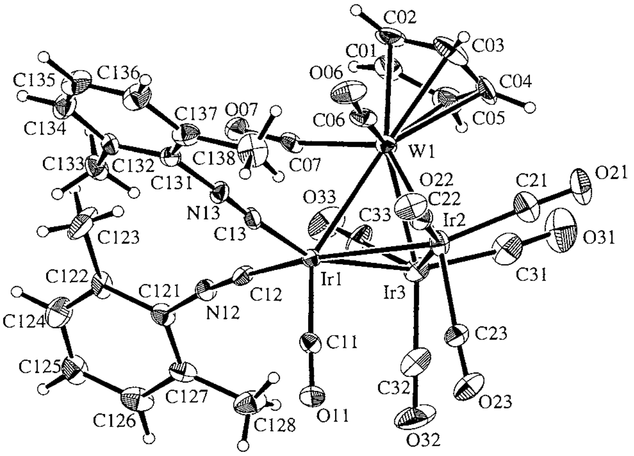


Fig. 2. Molecular structure and atomic labeling scheme for $[CpWIr_3(CO)_9(CNXy)_2]$ (**3**). 20% thermal envelopes are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

2.3. Solution structures

As mentioned above, the IR spectra of the complexes **3**, **4**, **6** and **7** are indicative of the presence of isomers, with the mono-(isocyanide) substituted derivatives displaying carbonyl frequencies arising from terminal carbonyls only. For all the clusters **2**-**7**, only IR absorptions appropriate for terminal isocyanide ligands are observed [ν(CN) 2179–2155 cm^{-1}] (this is not unexpected; previous studies have revealed that the electron withdrawing $R = CF_3$ group is required to encourage the CNR ligand to adopt an edge-bridging coordination mode [44]). These results, in combination with the structural characterization of **3**, lead us to postulate that the clusters **2** and **5** adopt structures with all-terminal ligand coordination geometries, analogous to the structurally characterized precursor cluster **1** [29], and the 'parent' cluster $[Ir_4(CO)_{12}]$ [45] and its mono-(isocyanide) substituted derivative $[Ir_4(CO)_{11}(CNBu^t)]$ [46]. The complexity of the IR spectra of **3**, **4**, **6** and **7** indicates the presence of isomers, weak absorptions in the bridging carbonyl region suggesting that the clusters exist as mixtures of isomers with all-terminal ligand geometries and isomers incorporating a plane of bridging carbonyls (Fig. 1). We have recently reported the isomer distribution and ligand fluxionality at $[CpWIr_3(\mu\text{-}CO)_3(CO)_{11-n}(L)_n]$ [$L = PPh_3$, PMe_3; $n = 1$, 2 [4]] and $[CpWIr_3(\mu\text{-}L)(\mu\text{-}CO)_3(CO)_6]$ [L = dppe, dppm [5]]. The IR spectra of **2**-**7** and unusual solid-state structure of **3** prompted us to investigate the isomer distribution and fluxionality of **5**-**7**. The ^{13}C-NMR spectra of **5**-**7** each display a single carbonyl resonance at r.t. Cooling the samples to 143 K reveals broadened resonances only, and solubility problems precluded a study at lower temperatures. The variable-temperature NMR results suggest that the carbonyls are undergoing much faster exchange than that observed in their phosphine-ligated analogues [4,5] (for which low temperature limiting spectra were obtained in the range 163–193 K).

2.4. Thermolyses of isocyanide-adducts of $[CpWIr_3(CO)_{11}]$

Thermolyses of isocyanide-ligated transition metal carbonyl clusters sometimes result in an increased 'metal loading' of the isocyanide ligand [47,48], and in one instance led to cleavage of the C≡NR bond [49]. With these results in mind, the thermolyses of **5** and **6** were investigated. However, rather than increasing the 'loading' of the isocyanide ligand, redistribution of isocyanide ligands resulted, affording mixtures of **5** and **6** in each case.

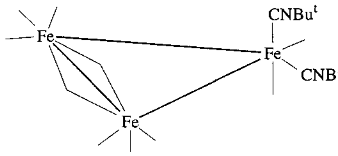


Fig. 3. Ref. [42].

2.5. Discussion

Stuntz and Shapley have examined isocyanide substitution at $[Ir_4(CO)_{12}]$ [50]. Introduction of ^{t}BuNC into the tetrairidium cluster necessitates significantly more forcing conditions (refluxing chlorobenzene or prior activation with $Me_3NO \cdot 2H_2O$) than are required to effect substitution at $[CpWIr_3(CO)_{11}]$ (**1**). We have noted a similar rate enhancement for phosphine substitution in proceeding from the homometallic to the heterometallic system. IR and ^{13}C-NMR spectra for $[Ir_4(CO)_{12-n}(CNR)_n]$ are consistent with isomers with terminal carbonyls only for $n = 1$ or 2, and isomers possessing bridging carbonyls for $n = 3$ or 4. A similar result is apparent for the tungsten–triiridium derivatives if the Cp group is considered as the first incoming ligand. Low temperature limiting spectra were achievable for the tetrairidium system at 183 K, but could not be obtained for the mixed-metal derivatives to 143 K, consistent with significantly enhanced fluxionality from the homometallic to the heterometallic system. The structural study of $[Ir_4(CO)_{11}(CNBu^t)]$ revealed a derivative with no bridging carbonyl ligands, as expected from the solution spectral data [46]. The structural study of $[CpWIr_3(CO)_9(CNXy)_2]$ (**3**) similarly reveals an isomeric form with no bridging carbonyls, although the spectral data for this derivative indicate that other isomers with bridging carbonyls are also present in solution.

Cluster **3** is the first structurally characterized tetrahedral cluster with two terminal isocyanide groups ligated to the same metal vertex, although a precedent exists in trinuclear cluster chemistry: a structural characterization of the triangular $[Fe_3(\mu\text{-}CO)_2(CO)_8(CNBu^t)_2]$ reveals a related ligand disposition to **3** [42], with two ^{t}BuNC ligated to the same iron vertex, but with two bridging carbonyls ligating the Fe–Fe bond opposite the bis(isocyanide)-ligated iron vertex (Fig. 3).

3. Experimental

All reactions were performed under an atmosphere of dry nitrogen (high-purity grade, CIG), although no special precautions were taken to exclude air during work-up. The reaction solvents were dried and distilled under nitrogen using standard methods: CH_2Cl_2 over CaH_2, THF and toluene from sodium/benzophenone. All other solvents were reagent grade, and used as received. Petroleum ether refers to a fraction of boiling point range 60–80°C. The products of thin-layer chromatography were separated on 20 × 20 cm glass plates coated with Merck GF_{254} silica gel (0.5 mm). $[CpWIr_3(CO)_{11}]$ [28] was prepared by the published procedure. ^{13}CO-enriched samples were prepared from ^{13}CO-enriched (65%) **1**, itself obtained by stirring a solution of the cluster in CH_2Cl_2 under 1.2 atm ^{13}CO at 60°C for 48 h. *t*-Butylisocyanide (Aldrich) and 2,6-dimethylphenylisocyanide (Fluka) were purchased commercially and used as received.

IR spectra were recorded on a Perkin–Elmer System 2000 Fourier transform spectrophotometer with NaCl optics. ^{1}H-NMR spectra were recorded on a Varian Gemini 300 spectrometer (300 MHz) and were run in $CDCl_3$ (Aldrich) or acetone-d_6 (Aldrich). ^{13}C-NMR spectra were recorded on a Varian VXR300S spectrometer (75 MHz) in acetone-d_6 (Aldrich) or $4CS_2$:$1CD_2Cl_2$ (CS_2: Univer; CD_2Cl_2: Aldrich) or on a Bruker DMX 500, spectrometer (125.7 MHz) in $CDFCl_2$ [51]. Chemical shifts in ppm are referenced to internal residual solvent.

Mass spectra were obtained at the Australian National University on a VG ZAB 2SEQ instrument (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, matrix 3-nitrobenzyl alcohol). Peaks are reported in the form: m/z (assignment, relative intensity). Elemental microanalyses were performed by the Microanalysis Service Unit in the Research School of Chemistry, Australian National University.

3.1. Reaction of $[CpWIr_3(CO)_{11}]$ with one equivalent of XyNC

An orange solution of $[CpWIr_3(CO)_{11}]$ (**1**) (20.0 mg, 0.0176 mmol) and XyNC (2.3 mg, 0.0176 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 16 h. The dark orange solution was then evaporated to dryness. The resultant orange residue was dissolved in CH_2Cl_2 (ca. 1 ml) and chromatographed ($2CH_2Cl_2$:1 petroleum ether eluant), affording two bands. The contents of the first band were identified as **1** (2.6 mg, 12%) by solution IR spectroscopy. Crystallization of the contents of the second band, R_f 0.60, from CH_2Cl_2/MeOH afforded orange crystals of $[CpWIr_3(CO)_{10}(CNXy)]$ (**2**) (13.6 mg, 60%). Analytical data for **2**: IR (c-C_6H_{12}): ν(C≡N) 2153m, ν(C≡O) 2067s, 2037vs, 2027m, 2014s, 2001w, 1987w, 1986m, 1972w, 1950w cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.17–7.09 (m, 3H, C_6H_3), 5.21 (s, 5H, C_5H_5), 2.38 (s, 6H, Me); MS 1237 ($[M]^+$, 10), 1209 ($[M-CO]^+$, 12), 1181 ($[M-2CO]^+$, 25), 1153 ($[M-3CO]^+$, 100), 1125 ($[M-4CO]^+$, 55), 1097 ($[M-5CO]^+$, 39), 1069 ($[M-6CO]^+$, 45), 1041 ($[M-7CO]^+$, 52), 1013 ($[M-8CO]^+$, 56), 985 ([$M-$

9CO]$^+$, 26). Anal. Calc.: C 23.31, H 1.14, N 1.13. Found: C 24.22, H 1.08, N 1.26%.

3.2. Reaction of [CpWIr$_3$(CO)$_{11}$] with two equivalents of XyNC

Following the method of Section 3.1, [CpWIr$_3$(CO)$_{11}$] (**1**) (20.0 mg, 0.0176 mmol) and XyNC (4.6 mg, 0.0352 mmol) in CH$_2$Cl$_2$ (20 ml) afforded two bands after chromatography (2CH$_2$Cl$_2$:1 petroleum ether eluant). The contents of the first band were identified as **2** (6.5 mg, 30%) by solution IR spectroscopy. Crystallization of the contents of the second band, R_f 0.38, from CH$_2$Cl$_2$/MeOH afforded orange crystals of [CpWIr$_3$(CO)$_9$(CNXy)$_2$] (**3**) (11.1 mg, 47%). Analytical data for **3**: IR (c-C$_6$H$_{12}$): ν(C≡N) 2152m, 2118m, ν(C≡O) 2051s, 2046m, 2027vs, 2025vs, 2007s, 2001s, 1994m, 1991m, 1984m, 1978m, 1898w, 1847w cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.30–7.03 (m, 6H, C$_6$H$_3$), 5.08 (s, 5H, C$_5$H$_5$), 2.35 (s, 12H, Me); MS 1340 ([M]$^+$, 5), 1312 ([$M-$CO]$^+$, 6), 1284 ([$M-$2CO]$^+$, 14), 1256 ([$M-$3CO]$^+$, 100), 1228 ([$M-$4CO]$^+$, 58), 1200 ([$M-$5CO]$^+$, 42), 1172 ([$M-$6CO]$^+$, 23), 1144 ([$M-$7CO]$^+$, 19), 1116 ([$M-$8CO]$^+$, 16). Anal. Calc.: C 28.68, H 1.73, N 2.09. Found: C 28.19, H 1.83, N 2.04%.

3.3. Reaction of [CpWIr$_3$(CO)$_{11}$] with three equivalents of XyNC

Following the method of Section 3.1, [CpWIr$_3$(CO)$_{11}$] (**1**) (20.0 mg, 0.0176 mmol) and XyNC (7.0 mg, 0.0530 mmol) in CH$_2$Cl$_2$ (20 ml) afforded two bands after chromatography (3 CH$_2$Cl$_2$:1 petroleum ether eluant). The contents of the first band were identified as **3** (6.6 mg, 28%) by solution IR spectroscopy. Crystallization of the contents of the second band, R_f 0.55, from CH$_2$Cl$_2$/MeOH afforded orange crystals of [CpWIr$_3$(CO)$_8$(CNXy)$_3$] (**4**) (16.0 mg, 63%). Analytical data for **4**: IR (c-C$_6$H$_{12}$): ν(C≡N) 2150s, 2131s, 2115s, ν(C≡O) 2031s, 2022m, 2017m, 1995vs, 1986s, 1972m, 1898w, 1879m, 1840m cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.12–7.00 (m, 9H, C$_6$H$_3$), 5.01 (s, 5H, C$_5$H$_5$), 2.31 (s, 18H, Me); MS 1443 ([M]$^+$, 8), 1415 ([$M-$CO]$^+$, 4), 1387 ([$M-$2CO]$^+$, 10), 1359 ([$M-$3CO]$^+$, 100), 1331 ([$M-$4CO]$^+$, 53), 1303 ([$M-$5CO]$^+$, 69), 1275 ([$M-$6CO]$^+$, 13), 1247 ([$M-$7CO]$^+$, 30). Satisfactory microanalyses could not be obtained due to sample decomposition in solution over days.

3.4. Reaction of [CpWIr$_3$(CO)$_{11}$] with one equivalent of ^{t}BuNC

Following the method of Section 3.1, [CpWIr$_3$(CO)$_{11}$] (**1**) (20.0 mg, 0.0176 mmol) and ^{t}BuNC (2 µl, 0.0176 mmol) in CH$_2$Cl$_2$ (20 ml) afforded two bands after chromatography (3CH$_2$Cl$_2$:2 petroleum ether eluant). The contents of the first band were identified as **1** (1.8 mg, 9%) by solution IR spectroscopy. Crystallization of the contents of the second band, R_f 0.78, from CH$_2$Cl$_2$/MeOH afforded orange crystals of [CpWIr$_3$(CO)$_{10}$(CNBu^t)] (**5**) (12.1 mg, 58%). Analytical data for **5**: IR (c-C$_6$H$_{12}$): ν(C≡N) 2178m, ν(C≡O) 2069s, 2036vs, 2026s, 2012s, 1999w, 1989sh, 1984m, 1964w cm^{-1}; ^{1}H-NMR (acetone-d_6): δ 5.44 (s, 5H, C$_5$H$_5$), 1.52 (s, 9H, Me); ^{13}C-NMR (acetone-d_6): 180.4 (s, CO), 87.6 (s, C$_5$H$_5$), other signals not observed; MS 1189 ([M]$^+$, 5), 1161 ([$M-$CO]$^+$, 10), 1133 ([$M-$2CO]$^+$, 20), 1105 ([$M-$3CO]$^+$, 100), 1077 ([$M-$4CO]$^+$, 55), 1049 ([$M-$5CO]$^+$, 30), 1021 ([$M-$6CO]$^+$, 37), 993 ([$M-$7CO]$^+$, 35), 965 ([$M-$8CO]$^+$, 22), 937 ([$M-$9CO]$^+$, 13). Anal. Calc.: C 20.21 H 1.19, N 1.13. Found: C 21.14, H 1.42, N 1.32%.

3.5. Reaction of [CpWIr$_3$(CO)$_{11}$] with two equivalents of ^{t}BuNC

Following the method of Section 3.1, [CpWIr$_3$(CO)$_{11}$] (**1**) (20.0 mg, 0.0176 mmol) and ^{t}BuNC (4 µl, 0.0352 mmol) in CH$_2$Cl$_2$ (20 ml) afforded two bands after chromatography (3CH$_2$Cl$_2$:2 petroleum ether eluant). The contents of the first band were identified as **5** (5.6 mg, 28%) by solution IR spectroscopy. Crystallization of the contents of the second band, R_f 0.39, from CH$_2$Cl$_2$/MeOH afforded orange crystals of [CpWIr$_3$(CO)$_9$(CNBu^t)$_2$] (**6**) (12.6 mg, 58%). Analytical data for **6**: IR (c-C$_6$H$_{12}$): ν(C≡N) 2177m, 2152m, ν(C≡O) 2049s, 2045s, 2022vs, 2005s, 1996s, 1986s, 1974m, 1925w, 1890m, 1854w, 1838w cm^{-1}; ^{1}H-NMR (acetone-d_6): δ 5.18 (s, 5H, C$_5$H$_5$), 1.49 (s, 18H, Me); ^{13}C-NMR (CS$_2$/CD$_2$Cl$_2$): 182.0 (s, CO), 86.2 (s, C$_5$H$_5$), 28.5 (s, Me), other signals not observed; MS 1244 ([M]$^+$, 5), 1216 ([$M-$CO]$^+$, 7), 1188 ([$M-$2CO]$^+$, 17), 1160 ([$M-$3CO]$^+$, 100), 1132 ([$M-$4CO]$^+$, 65), 1104 ([$M-$5CO]$^+$, 47), 1076 ([$M-$6CO]$^+$, 28), 1048 ([$M-$7CO]$^+$, 23), 1020 ([$M-$8CO]$^+$, 21), 992 ([$M-$9CO]$^+$, 20). Anal. Calc.: C 23.17 H 1.86, N 2.25. Found: C 23.51, H 1.98, N 2.00%.

3.6. Reaction of [CpWIr$_3$(CO)$_{11}$] with three equivalents of ^{t}BuNC

Following the method of Section 3.1, [CpWIr$_3$(CO)$_{11}$] (**1**) (20.0 mg, 0.0176 mmol) and ^{t}BuNC (6 µl, 0.0530 mmol) in CH$_2$Cl$_2$ (20 ml) afforded two bands after chromatography (2CH$_2$Cl$_2$:1 petroleum ether eluant). The contents of the first band were identified as **6** (6.1 mg, 28%) by solution IR spectroscopy. Crystallization of the contents of the second band, R_f 0.38, from CH$_2$Cl$_2$/MeOH afforded orange crystals of [CpWIr$_3$(CO)$_8$(CNBu^t)$_3$] (**7**) (13.5 mg, 59%). Analytical data for **7**: IR (CH$_2$Cl$_2$): ν(C≡N) 2179m, 2155m,

ν(C≡O) 2056vw, 2021vs, 1982vs, 1867w, 1816m cm^{-1}; ^{1}H-NMR (acetone-d_6): δ 4.99 (s, 5H, C_5H_5), 1.46 (s, 27H, Me); ^{13}C-NMR (CS_2/CD_2Cl_2) 182.6 (s, CO), 85.9 (s, C_5H_5), 29.0 (s, Me), other signals not observed; MS 1299 ($[M]^+$, 10), 1271 ($[M-CO]^+$, 6), 1243 ($[M-2CO]^+$, 13), 1215 ($[M-3CO]^+$, 100), 1187 ($[M-4CO]^+$, 60), 1159 ($[M-5CO]^+$, 75), 1131 ($[M-6CO]^+$, 18), 1103 ($[M-7CO]^+$, 35), 1075 ($[M-8CO]^+$, 30). Satisfactory microanalyses could not be obtained due to sample decomposition in solution over days.

3.7. Thermolysis of [$CpWIr_3(CO)_{10}(CNBu^t)$]

An orange solution of [$CpWIr_3(CO)_{10}(CNBu^t)$] (**5**) (20.0 mg, 0.0168 mmol) in THF (15 ml) was slowly heated to 60°C and refluxed for 30 h. A brown decomposition product was noted in the resultant orange solution. The solution was cooled and the solvent removed in vacuo, leaving a brown residue. Subsequent purification by thin layer chromatography ($2CH_2Cl_2$:1 petroleum ether eluant) afforded two bands, identified by IR spectroscopy as **5** (3.3 mg, 15%) and [$CpWIr_3(CO)_9(CNBu^t)_2$] (**6**) (2.0 mg, 10%).

3.8. Thermolysis of [$CpWIr_3(CO)_9(CNBu^t)_2$] (method A)

An orange solution of [$CpWIr_3(CO)_9(CNBu^t)_2$] **6** (20.0 mg, 0.0164 mmol) in THF (15 ml) was slowly heated to 60°C and refluxed for 30 h. The green solution obtained was evaporated to dryness. Subsequent purification by thin layer chromatography ($2CH_2Cl_2$:1 petroleum ether eluant) afforded two bands, identified by IR spectroscopy as **5** (2.0 mg, 10%) and **6** (7 mg, 30%).

3.9. Thermolysis of [$CpWIr_3(CO)_9(CNBu^t)_2$] (method B)

An orange solution of [$CpWIr_3(CO)_9(CNBu^t)_2$] **6** (20.0 mg, 0.0160 mmol) in toluene (15 ml) was slowly heated to 110°C and refluxed for 30 h. The brown solution obtained was evaporated to dryness. Purification by thin layer chromatography ($3CH_2Cl_2$:1 petroleum ether eluant) afforded three minor bands, identified by IR spectroscopy as **5** (2.3 mg, 12%), **6** (6.0 mg, 30%) and [$CpWIr_3(CO)_8(CNBu^t)_3$] (**7**) (1.6 mg, 8%).

3.10. Structure determination

Crystals of compound **3** suitable for diffraction analysis were grown by slow diffusion of methanol into dichloromethane at r.t. A unique diffractometer data set was measured at ~295 K within the specified $2\theta_{max}$ limit (ω–2θ scan mode; monochromatic Mo–K_α radiation ($\lambda = 0.7107_3$ Å)), yielding N independent reflections. N_o of these with $I = 3\sigma(I)$ were considered 'observed' and used in the full matrix/large block least squares refinements after empirical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included, constrained at estimated values. Conventional residuals R, R_w on $|F|$ at convergence are given. Neutral atom complex scattering factors were used, computation using teXsan [52]. Pertinent results are given in the figures and tables.

4. Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank the Australian Research Council for support of this work and Johnson-Matthey Technology Center for the generous loan of $IrCl_3$. Associate Professor O.b. Shawkataly is thanked for the gift of some 2,6-dimethylphenylisocyanide. MGH is an ARC Australian Research Fellow.

References

[1] Part XI: S.M. Waterman, V.-A. Tolhurst, M.G. Humphrey, M.I. Bruce, P.J. Low, D.C.R. Hockless, Organometallics 17 (1998) 5789.

[2] E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Pergamon Press, Oxford, UK, 1995.

[3] G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, UK, 1982.

[4] S.M. Waterman, M.G. Humphrey, Organometallics (1998), submitted for publication.

[5] S.M. Waterman, M.G. Humphrey, D.C.R. Hockless, J. Organomet. Chem. 565 (1998) 81.

[6] S.M. Waterman, M.G. Humphrey, D.C.R. Hockless, J. Organomet. Chem. 555 (1998) 25.

[7] N.T. Lucas, M.G. Humphrey, P.C. Healy, M.L. Williams, J. Organomet. Chem. 545 (1997) 519.

[8] N.T. Lucas, I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, M.P. Seneka Perera, M.L. Williams, J. Organomet Chem. 540 (1997) 147.

[9] S.M. Waterman, M.G. Humphrey, V.-A. Tolhurst, B.W. Skelton, A.H. White, Organometallics 15 (1996) 934.

[10] J. Lee, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, Organometalllics 12 (1993) 3468.
[11] V. Albano, P. Bellon, V. Scatturin, Chem. Commun. (1967) 730.
[12] A.J. Drakesmith, R. Whyman, J. Chem. Soc. Dalton Trans. (1973) 362.
[13] K.J. Karel, J.R. Norton, J. Am. Chem. Soc. 96 (1974) 6812.
[14] G.F. Stuntz, J.R. Shapley, Inorg. Chem. 15 (1976) 1994.
[15] G.F. Stuntz, J.R. Shapley, J. Am. Chem. Soc. 99 (1977) 607.
[16] D.J. Darensbourg, B.J. Baldwin-Zuschke, Inorg. Chem. 20 (1981) 3846.
[17] F. Demartin, M. Manassero, M. Sansoni, L. Garlaschelli, U. Sartorelli, J. Organomet. Chem. 204 (1981) C10.
[18] B.E. Mann, C.M. Spencer, A.K. Smith, J. Organomet. Chem. 244 (1983) C17.
[19] A.J. Blake, A.G. Osborne, J. Organomet. Chem. 260 (1984) 227.
[20] J.A. Clucas, M.M. Harding, B.S. Nicholls, A.K. Smith, J. Chem. Soc. Chem. Commun. (1984) 319.
[21] M.M. Harding, B.S. Nicholls, A.K. Smith, Acta. Crystallogr. C40 (1984) 790.
[22] V.G. Albano, D. Braga, R. Ros, A. Scrivanti, J. Chem. Soc. Chem. Commun. (1985) 866.
[23] R. Ros, A. Scrivanti, V.G. Albano, D. Braga, J. Chem. Soc. Dalton Trans. (1986) 2411.
[24] D. Braga, F. Grepioni, G. Guadalupi, A. Scrivanti, R. Ros, R. Roulet, Organometallics 6 (1987) 56.
[25] M. Bojczuk, B.T. Heaton, S. Johnson, C.A. Ghilardi, A. Orlandini, J. Organomet. Chem. 341 (1988) 473.
[26] M.H.A. Benvenutti, P.B. Hitchcock, J.F. Nixon, M.D. Vargas, J. Chem. Soc. Dalton Trans. (1996) 739.
[27] K. Besançon, G. Laurenczy, T. Lumini, R. Roulet, Helv. Chim. Acta 76 (1993) 2926.
[28] J.R. Shapley, S.J. Hardwick, D.S. Foose, G.D. Stucky, J. Am. Chem. Soc. 103 (1981) 7383.
[29] M.R. Churchill, J.P. Hutchinson, Inorg. Chem. 20 (1981) 4112.
[30] U. Flörke, H.-J. Haupt, Zeit. Kristallogr. 191 (1990) 149.
[31] A. Strawczynski, R. Ros, R. Roulet, D. Braga, C. Gradella, F. Grepioni, Inorg. Chim. Acta 170 (1990) 17.
[32] E. Galdecka, Z. Galdecki, K. Wajda-Hermanowicz, F.P. Pruchnik, J. Chem. Cryst. 25 (1995) 717.
[33] D.J. Darensbourg, B.J. Baldwin-Zuschke, J. Am. Chem. Soc. 104 (1982) 3906.
[34] M.I. Bruce, D. Schultz, R.C. Wallis, A.D. Redhouse, J. Organomet. Chem. 169 (1979) C15.
[35] A. Rivera, G.A. Sheldrick, M.B. Hrsthouse, Acta Crystallogr. B34 (1978) 1985.
[36] G.A. Orpen, G.M. Sheldrick, Acta Crystallogr. B34 (1978) 1989.
[37] M.R. Churchill, F.J. Hollander, Inorg. Chem. 19 (1980) 306.
[38] M.I. Bruce, T.W. Hambly, B.K. Nicholson, J. Chem. Soc. Dalton Trans. (1983) 2385.
[39] M.I. Bruce, J.G. Matisons, R.C. Wallis, J.M. Patrick, B.W. Stelton, A.H. White, J. Chem. Soc. Dalton Trans. (1983) 2365.
[40] I. Brüdgam, H. Hartl, D. Lentz, Z. Naturforsch 39b (1984) 721.
[41] M.I. Bruce, G.N. Pain, C.A. Hughes, J.M. Patrick, B.W. Skelton, A.H. White, J. Organomet. Chem. 307 (1986) 343.
[42] J.B. Murray, B.K. Nicholson, A.J. Whitton, J. Organomet. Chem. 385 (1990) 91.
[43] A.J. Deeming, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon Press, Oxford, 1995, p. 4.
[44] D. Lentz, Angew. Chem. Int. Ed. Engl. 33 (1994) 1315.
[45] M.R. Churchill, J.P. Hutchinson, Inorg. Chem. 17 (1978) 3528.
[46] M.R. Churchill, J.P. Hutchinson, Inorg. Chem. 18 (1979) 2451.
[47] M.I. Bruce, J.G. Matisons, J.R. Rodgers, R.C. Wallis, J. Chem. Soc. Chem. Commun. (1981) 1070.
[48] D. Lentz, R. Marschall, Chem. Ber. 124 (1991) 497.
[49] R.D. Adams, P. Mathur, B.E. Segmüller, Organometallics 2 (1983) 1258.
[50] G.F. Stuntz, J.R. Shapley, J. Organomet. Chem. 213 (1981) 389.
[51] J.S. Siegel, F.A.L. Anet, J. Org. Chem. 53 (1988) 2629.
[52] texsan: Single Crystal Structure Analysis Software, Version 1.7-3, Molecular Structure Corporation, The Woodlands, TX, USA, 1995.