

## SYNTHESIS AND STEREOCHEMISTRY OF MONO- AND DI-OLEFIN DERIVATIVES OF TETRAIRIDIUM CARBONYL CLUSTERS

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### Summary

The reactions of  $\text{NEt}_4[\text{Ir}_4(\text{CO})_{11}\text{Br}]$  (I) with ethylene, cyclopropene, 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene and bicyclo[2.2.1]hept-2-ene in the presence of  $\text{AgBF}_4$  gave high yields of  $\text{Ir}_4(\text{CO})_{11}$ (olefin) (II–V), in which the olefin is bonded in an axial position on a basal Ir atom. The mono-olefin in II–V is quantitatively displaced by CO giving  $\text{Ir}_4(\text{CO})_{12}$  or by  $\text{SO}_2$  giving  $\text{Ir}_4(\text{CO})_{11}(\text{SO}_2)$ . The reaction of I with bicyclo[2.2.1]hepta-2,5-diene, cycloocta-1,5-diene or cyclooctatetraene in the presence of  $\text{AgBF}_4$  gave  $\text{Ir}_4(\text{CO})_{10}(\eta^4\text{-polyolefin})$ , the first substitution taking place preferentially at an axial site giving  $\text{Ir}_4(\text{CO})_{11}(\eta^2\text{-polyolefin})$ , followed by chelation on a radial site of the same metal center. All the above clusters are fluxional at room temperature.

### Introduction

The low solubility of  $\text{Ir}_4(\text{CO})_{12}$  in organic solvents below 100°C is a severe restriction for an extensive investigation of its substitution reactions [2–6]. However, above 40°C the carbonyl ligands may be replaced by good donor ligands such as phosphines, arsines or isonitriles, as shown by several kinetic studies [6–9]. Hitherto the only detailed study of the reaction of  $\text{Ir}_4(\text{CO})_{12}$  with olefins was that reported by Shapley et al. [10]. These authors showed that the thermal reaction of  $\text{Ir}_4(\text{CO})_{12}$  with cycloocta-1,5-diene (1,5-cod) provides a complex mixture of organoiridium clusters containing  $\text{Ir}_4(\text{CO})_5(\text{C}_8\text{H}_{12})_2(\text{C}_8\text{H}_{10})$  and  $\text{Ir}_7(\text{CO})_7(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$  as major products. Thus the drastic conditions required for substitution mainly promote the activation of C–H bonds in the unsaturated organic substrates [10,11]. However, the use of  $\text{Me}_3\text{NO}$  as an oxidative decarbonylating reagent allowed

formation of the derivatives  $\text{Ir}_4(\text{CO})_{12-2x}(\text{C}_8\text{H}_{12})_x$  ( $x = 1-3$ ) under relatively mild conditions.

In the course of an investigation [12] of the chemistry of the iridium cluster  $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$  (I) [13], we have found that this anion is ideally suited as a starting material for selective mono-substitution of CO by olefins, and we report here on the synthesis and characterization of clusters of general formula  $\text{Ir}_4(\text{CO})_{11}(\text{olefin})$  and  $\text{Ir}_4(\text{CO})_{12-2x}(\text{diolefin})_x$  ( $x = 1, 2$ ).

## Results and discussion

Bromide abstraction from I with one equivalent  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2$  under ethylene (1 atm) proceeded readily at  $-28^\circ\text{C}$  giving  $\text{Ir}_4(\text{CO})_{11}(\text{C}_2\text{H}_4)$  (II, 76%) as thermally unstable yellow microcrystals. The same reaction in dimethyl ether containing an excess of cyclopropene, 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene or bicyclo[2.2.1]hept-2-ene afforded  $\text{Ir}_4(\text{CO})_{11}(\text{C}_3\text{H}_4)$  (III, 63%),  $\text{Ir}_4(\text{CO})_{11}(\text{C}_8\text{H}_8\text{O})$  (IV, 71%) and  $\text{Ir}_4(\text{CO})_{11}(\text{C}_7\text{H}_{10})$  (V, 74%), respectively. The ethylene cluster II is the least stable and tends to decompose as a solid or in solution above  $-30^\circ\text{C}$  in the absence of free ethylene. The three other clusters are yellow solids, which are stable when stored  $< 0^\circ\text{C}$  under nitrogen. They are soluble in most organic solvents, but slowly decompose in chlorinated solvents above  $-20$  (V),  $0$  (III) or  $25^\circ\text{C}$  (IV). The higher stability of the clusters with strained olefins parallels the pattern generally observed for complexes of  $\text{Ni}^0$  [14],  $\text{Pd}^0$  and  $\text{Pt}^0$  [15], and is partially reflected in the higher  $^1\text{H}$  coordination chemical shift  $\Delta\delta = \delta(\text{ligand}) - \delta(\text{complex})$  observed in III (6.5) relative to II (1.88 ppm).

The  $^1\text{H}$  NMR spectrum of IV (Table 1) is temperature invariant up to 310 K, suggesting the presence of a single stereoisomer (radial vs. axial coordination of the double bond to the cluster). We propose an axial coordination of the double bond in II-V from a comparison of the low-temperature  $^{13}\text{C}$  NMR spectra with those of the  $\text{Ir}_4(\text{CO})_{11}(\text{PEt}_3)$  isomers [16] and with that of VII. The spectrum of cluster V (Table 2) resembles closely that of the axial isomer of  $\text{Ir}_4(\text{CO})_{11}(\text{PEt}_3)$  with signals at  $\delta$  205.1 (intensity 2; bridging CO's), 195.5 (1; bridging CO), 170.8 (2), 170.1 (1), 155.6 (2), 155.5 (1) and 154.3 ppm (2). Signals at  $\delta$  170-175 ppm are due to radial CO's [16]. Since signals corresponding to 3 CO's are observed in this region, carbonyl f (formula in Table 2) must be radial and, consequently, the double bond is in an axial position. This is consistent with the signal corresponding to 2 CO's observed at  $\delta$  170.6 ppm for VII in which a C=C bond has replaced carbonyl f.

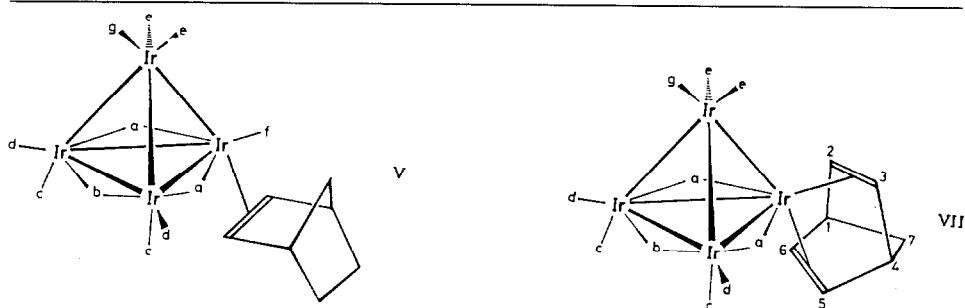
The *exo*-coordination of the metal in IV (with respect to the roof-shaped ligand) is revealed by the magnitude of the proton coupling constant between H(1) (bridge-head proton) and H(2) (olefinic proton) relative to that in the free ligand. The H(2) resonance appears as a singlet in IV (width at half-height 0.9 Hz; resolution 0.3 Hz). The sum of coupling constants involving H(2) ( $J < 0.6$  Hz) is smaller than  $J_{1,2}$  in the free ligand (1.1 Hz). Thus H(2) and H(3) must be somewhat pushed over toward the *endo*-side of the ligand in IV, and this is the expected effect of coordination of the metal in the *exo*-position (as verified by the crystal structure determination on  $\text{Fe}_2(\text{CO})_7(\text{C}_8\text{H}_8\text{O})$  [17]). A similar argument was used to assign the *exo*-coordination of the metal in V. The tendency of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene to coordinate through the *exo*-face of its endocyclic double bond seems to be quite general (for other examples, see [18]). A prior example of *exo*-coordination to bicyclo[2.2.1]hept-2-ene is also known [15].

TABLE 1  
<sup>1</sup>H NMR DATA <sup>a</sup> OF CLUSTERS Ir<sub>4</sub>(CO)<sub>11</sub>(η<sup>2</sup>-olefin)

Cluster	T (K)	δ(H) (ppm)	J (Hz)	Assignment	Δδ (ppm) <sup>b</sup>
II	230	3.55 s			1.88
III	230	3.64 dt 1.10 dd 0.82 dt	6.8 (1, 3a) 2.6 (1, 3s) 2.9 (3a, 3s)	3a 1, 2 3s	6.50
IV	240	5.49 s 5.39 s 5.13 s 4.23 s	< 0.5 (1, 2)	Z E 1, 4 2, 3	2.24
V	230	4.05 bs 2.84 bs 1.70 dd 1.45 d 0.93 dd 0.84 d		2, 3 1, 4 8 (5x, 5n) 9.5 (7a, 7s) 2 (5x, 6n) 7s	1.95
VI	190	6.54 s 4.90 s 3.43 s 2.24 d 2.00 d	8.7 (7a, 7s)	5, 6 2, 3 1, 4 7a 7s	1.85

<sup>a</sup> 360 MHz; CDCl<sub>3</sub> for I and III, CD<sub>2</sub>Cl<sub>2</sub> for II, IV and V; δ relative to TMS. <sup>b</sup> Δδ = δ(ligand) - δ(complex) for olefinic protons.

TABLE 2  
 $^{13}\text{C}$  NMR DATA<sup>a</sup> FOR V AND VII



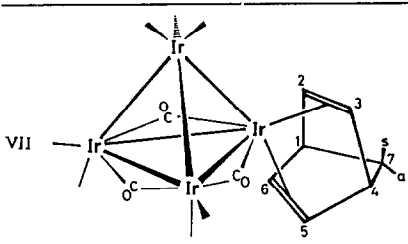
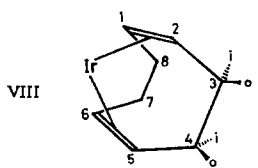
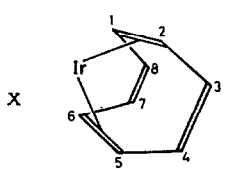
$\delta(\text{CO})$ (ppm) <sup>b</sup>	Ratio	Assignment	$\delta(\text{CO})$ (ppm) <sup>b,c</sup>	Ratio	Assignment
205.1	2	a	207.5	2	a
195.5	1	b	198.1	1	b
170.8	2	d	170.6	2	d
170.1	1	f	158.7	2	e or c
155.6	2	e or c	151.8	2	c or e
155.5	1	g	151.5	1	g
154.3	2	c or e			

<sup>a</sup> 90.55 MHz;  $\text{CD}_2\text{Cl}_2$ ;  $\delta$  relative to TMS. <sup>b</sup> At 190 K. <sup>c</sup> At 300 K;  $\delta(\text{C})$  172.2 (br. s., CO), 68.2 (t, C(7)), 54.8 (d, C=C), 47.6 (d, C(1, 4)).

Carbon monoxide (1 atm) quantitatively displaces the mono-olefins in II–V to give  $\text{Ir}_4(\text{CO})_{12}$ . Bubbling  $\text{SO}_2$  through a solution of V in  $\text{CH}_2\text{Cl}_2$  gave  $\text{Ir}_4(\text{CO})_9(\mu\text{-CO})_2(\mu\text{-SO}_2)$  [19], but no further CO displacement from the latter occurred even in liquid  $\text{SO}_2$ .

The reaction of I with excess bicyclo[2.2.1]hepta-2,5-diene (nbd) at  $-28^\circ\text{C}$  in the presence of  $\text{AgBF}_4$  (1 equivalent) gave (after filtration to remove  $\text{AgBr}$ ) a yellow solution of product VI, which could not be isolated in the solid state but whose IR spectrum ( $\text{CH}_2\text{Cl}_2$ ) was identical to that of IV in the  $\nu(\text{CO})$  region. The  $^1\text{H}$  NMR spectrum of IV ( $\text{CD}_2\text{Cl}_2$ , 190 K) presents two signals, at  $\delta$  6.54 and 4.90 ppm, attributable to the olefinic protons of the uncoordinated ( $\delta$  6.75 ppm in free nbd) and coordinated double bonds, respectively. Cluster VI is thus the monomeric  $\text{Ir}_4(\text{CO})_{11}(\eta^2\text{-nbd})$  (and not the bridged  $\text{Ir}_4(\text{CO})_{11}(\mu\text{-nbd})\text{Ir}_4(\text{CO})_{11}$  as previously proposed [1]). Disproportionation of VI took place upon warming the yellow solution at  $30^\circ\text{C}$ , as evidenced by the precipitation of insoluble  $\text{Ir}_4(\text{CO})_{12}$  and by the appearance of new IR signals attributable to the disubstituted cluster VII. The olefinic signals of VII now appear at  $\delta(\text{H})$  4.61 and 3.95 ppm (Table 3). The latter is attributed to the double bond coordinated in an axial position, since in all reported  $\text{M}_4(\text{CO})_{12-x}\text{L}_x$  ( $\text{M} = \text{Ir}, \text{Rh}, \text{Co}$ ) [16,20–25] the chemical shift ( $^{13}\text{C}$  or  $^{31}\text{P}$  NMR) of a radially coordinated ligand always appears at lower field than an axially coordinated CO or  $\text{PR}_3$  ligand. The two double bonds must be coordinated to the same metal center, since a single signal at  $\delta(\text{C})$  170.6 ppm ( $\text{CD}_2\text{Cl}_2$ , 190 K) is observed for carbonyl d. Thus substitution by a diolefin takes place preferentially at an axial site, and chelation on a radial site of the same metal follows.

TABLE 3  
 $^1\text{H}$  NMR DATA <sup>a</sup> OF CLUSTERS  $\text{Ir}_4(\text{CO})_{10}(\eta^4\text{-polyolefin})$

Cluster	$\delta(\text{H})$ (ppm)		Assign- ment	$\Delta\delta$ (ppm)
	190K	300K		
	4.49 bs	4.51 m <sup>c</sup>	1, 4	2.14 2.80
	4.61 bs	4.27 m <sup>c</sup>	2, 3	
	3.95 bs		5, 6	
	1.17 d <sup>b</sup>	1.17 m <sup>c</sup>	7 s	
	1.13		7 a	
	4.55 m	3.98 m	1, 2	1.07
	3.29 m		5, 6	2.27
	3.00 m <sup>d</sup>		3o, 8o	
	2.49 m	2.78 m	4o, 7o	
	2.15 m		3i, 8i	
	1.82 m <sup>d</sup>	2.00 m	4i, 7i	
	6.47 d <sup>e</sup>	6.19 s	3, 8	0.68 <sup>f</sup> 1.64 <sup>f</sup>
	5.92 d <sup>e</sup>		4, 7	
	5.10 s	4.62 s	1, 2	
	4.14 s		5, 6	

<sup>a</sup> 360 MHz;  $\text{CD}_2\text{Cl}_2$ ;  $\delta$  relative to TMS. <sup>b</sup>  $J(7a, 7s)$  7 Hz. <sup>c</sup> Simulation as  $A_2MM'XX'$  spin system gave  $J(1, 2)$  2.5,  $J(1, 3)$  1.7,  $J(1, 7)$  1.4 Hz and  $J(2, 7) < 0.5$  Hz. <sup>d</sup>  $J(4i, 3i) \sim 12$  Hz. <sup>e</sup>  $J(3, 4) = J(7, 8)$  7.6 Hz. <sup>f</sup> with  $\delta(\text{free cot})$  5.78 at 300 K.

Clusters  $\text{Ir}_4(\text{CO})_{10}(1,5\text{-cod})$  (VIII) and  $\text{Ir}_4(\text{CO})_8(1,5\text{-cod})_2$  (IX) have been prepared by Shapley et al. [10] from  $\text{Ir}_4(\text{CO})_{12}$  (38 and 32% yields, respectively). The reaction of I with excess 1,5-cod and  $\text{AgBF}_4$  at  $-28^\circ\text{C}$  gave after filtration a yellow solution presumably containing  $\text{Ir}_4(\text{CO})_{11}(\eta^2\text{-}1,5\text{-cod})$  which was either warmed to  $30^\circ\text{C}$  to yield VIII (45%) (cf. formation of VII) or treated with  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  (2 mol-equiv.) to yield IX (38%) after column chromatography. The  $^1\text{H}$  NMR spectra of these two clusters have now been fully assigned by selective decoupling experiments (Table 3 and Experimental).

The reaction of I with excess cyclooctatetraene (cot) and  $\text{AgBF}_4$  gave, after work-up as for VII, the yellow cluster  $\text{Ir}_4(\text{CO})_{10}(\eta^4\text{-cot})$  (X, 20%). Treatment of a solution of X and an excess of cot in THF with  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  did not give any bis(cot) cluster.

All reported clusters show 3 IR bands characteristic of bridging CO's (Experimental). The IR spectrum of VII, VIII and X are very similar to that of  $\text{Ir}_4(\text{CO})_{10}(\text{Me}_2\text{AsC}_6\text{H}_4\text{AsMe}_2)$  [22] in which the bidentate ligand was shown by X-ray analysis to coordinate the same basal Ir atom [25]. The most relevant difference in the IR spectra between mono- and bis-substituted derivatives is the

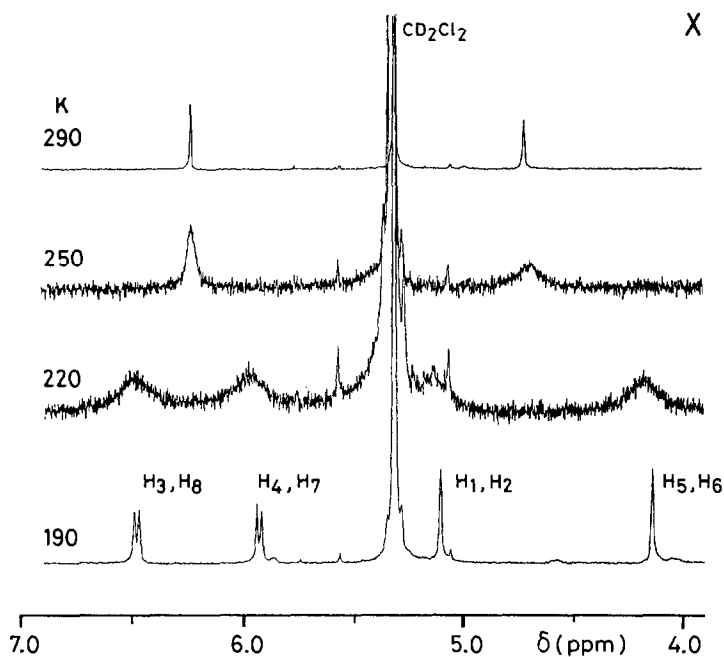


Fig. 1.  $^1\text{H}$  NMR (360 MHz) spectrum of  $\text{Ir}_4(\text{CO})_{10}(\eta^4\text{-cot})$  (X) in  $\text{CD}_2\text{Cl}_2$  at different temperatures.

lowering (ca.  $20\text{ cm}^{-1}$ ) of all  $\nu(\text{CO})$  frequencies on going from  $\text{Ir}_4(\text{CO})_{11}(\text{olefin})$  to  $\text{Ir}_4(\text{CO})_{10}(\text{diolefin})$ . A possible cause of this effect may be that the addition of a second non-carbonyl ligand increases the electron density on the whole  $\text{Ir}_4$  moiety, thereby increasing the  $\pi$ -back donation onto the remaining CO's. A similar shift to lower CO stretching frequencies was observed on going from  $\text{Ir}_4(\text{CO})_{11}\text{L}$  to  $\text{Ir}_4(\text{CO})_{10}\text{L}_2$  (L = monodentate phosphine or 1/2 bidentate diphosphine) [26].

The low-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of VII, VIII and X indicate that the mid-points of the two coordinated C=C bonds reside on a mirror plane containing the apical Ir atom and one basal  $\mu\text{-CO}$ . Likewise in IX the two chelating diolefins are related by a mirror plane containing the apical Ir atom and the basal  $\text{Ir}(\text{CO})_2$  group [10].

Clusters VII, VIII and X are fluxional on the  $^1\text{H}$  NMR time scale. The radial and axial olefinic proton signals of VII coalesce at  $\delta(\text{H})$  4.27 ppm at ca. 230 K. Similarly, the low temperature  $^1\text{H}$  NMR spectrum of VIII presents 3 pairs of signals corresponding to the axially and radially located olefinic proton, the outer  $\text{CH}_2$ , and the inner  $\text{CH}_2$  protons, respectively. On warming to 260 K, each pair coalesces, to give 3 distinct signals without any interconversion between inner and outer  $\text{CH}_2$  protons (Table 3). Thus the axial-radial site exchange does not involve conformational changes of the coordinated diolefins. Likewise for X (Fig. 1), both pairs of proton signals due to the uncoordinated ( $\delta$  6.47 and 5.92 ppm) and the coordinated double bonds (5.10 and 4.14 ppm) coalesce separately at ca. 240 K. This is most probably due to intramolecular CO randomization processes interconverting the axial and radial sites such as those proposed for  $\text{Ir}_4(\text{CO})_{10}(\text{Me}_2\text{AsC}_6\text{H}_4\text{AsMe}_2)$  [22]. These processes are currently being studied by variable-temperature  $^{13}\text{C}$  NMR [27].

## Experimental

$\text{NEt}_4[\text{Ir}_4(\text{CO})_{11}\text{Br}](\text{I})$  [13], cyclopropene [28] and 5,6-dimethylidene-7-oxobicyclo[2.2.1]hept-2-ene [17] were prepared by published procedures. Unless otherwise stated, experiments were carried out under dry oxygen-free nitrogen using solvents dried and distilled under nitrogen. Bicyclo[2.2.1]hept-2,5-diene (nbd), cycloocta-1,5-diene (cod) and cycloocta-1,3,5,7-tetraene (cot) (Merck) were passed through alumina prior to use. Other reagents, silica gel (70–230 and 230–400 mesh) and preparative-scale TLC plates (20 × 20 × 0.2 cm) (Merck) were used as received.

Infrared spectra were recorded on Perkin–Elmer 597 and 983 spectrophotometers and were calibrated with cyclohexane (2138.5) and polystyrene (1601.4  $\text{cm}^{-1}$ ).  $^{13}\text{C}$  NMR spectra were recorded on a Bruker WH-360 (90.55 MHz) spectrometer.  $^1\text{H}$  NMR spectra were recorded on Bruker CXP-200 (200 MHz), Bruker WH-360 (360 MHz) and Varian FT-80A (80 MHz) spectrometers ( $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$  as internal reference,  $\delta$  7.27 and 5.32 ppm, respectively). Microanalyses were performed by the Institute of analytical chemistry (University of Padova). Samples of clusters enriched in  $^{13}\text{C}$  were prepared from I (20–30%  $^{13}\text{C}$ ).

### Preparations

*Undecacarbonyl(ethylene)tetrairidium (II)*. A suspension of I (160 mg, 0.124 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 ml) was stirred at  $-28^\circ\text{C}$  under ethylene (1 atm) as solid  $\text{AgBF}_4$  (27 mg, 0.14 mmol) was added. After 45 min the mixture containing solid  $\text{AgBr}$  was filtered through a silica gel pad (5 cm) and eluted with  $\text{CH}_2\text{Cl}_2$  (8 ml) at ca.  $-25^\circ\text{C}$ . Cooling the yellow filtrate to  $-78^\circ\text{C}$  under ethylene gave a mass of yellow microcrystals. These were washed with ethylene-saturated  $\text{CH}_2\text{Cl}_2$  (3 ml) at  $-78^\circ\text{C}$  and dried in a stream of ethylene to give  $\text{Ir}_4(\text{CO})_{11}(\text{C}_2\text{H}_4)$  (105 mg, 76%). II is thermally unstable and must be stored under nitrogen at  $-78^\circ\text{C}$ . Above  $-25^\circ\text{C}$  it decomposes rapidly in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ , giving insoluble  $\text{Ir}_4(\text{CO})_{12}$  and an unidentified green-brown product. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2099m, 2057vs, 2038vs, 2022s, 1847s br.

*Undecacarbonyl(cyclopropene)tetrairidium (III)*. An excess of cyclopropene was condensed into a solution of I (322 mg, 0.25 mmol) in dimethyl ether (70 ml) at  $-35^\circ\text{C}$ .  $\text{AgBF}_4$  (51 mg, 0.26 mmol) was added and the mixture was stirred for 20 min at  $-28^\circ\text{C}$ . Filtration through a precooled silica gel pad (10 cm), elution with cold pentane (50 ml), and evaporation in vacuo at  $-20^\circ\text{C}$  to ca. 3 ml afforded yellow microcrystals. Recrystallization from pentane at  $-25^\circ\text{C}$  gave  $\text{Ir}_4(\text{CO})_{11}(\text{C}_3\text{H}_4)$  (176 mg, 63%). Found: C, 15.4; H, 0.50.  $\text{C}_{14}\text{H}_4\text{O}_{11}\text{Ir}_4$  calcd.: C, 15.1; H, 0.36%. IR (cyclohexane):  $\nu(\text{CO})$  2102w, 2067vs, 2037s, 2028m, 2012m, 2004w, 1897m, 1857s. III is thermally unstable and must be stored under nitrogen at  $-20^\circ\text{C}$ . It is soluble in most organic solvents, but slowly decomposes above  $0^\circ\text{C}$ .

*Undecacarbonyl(bicyclo[2.2.1]hept-2-ene)tetrairidium (V)*.  $\text{AgBF}_4$  (56 mg, 0.29 mmol) was added to a solution of I (353 mg, 0.27 mmol) and bicyclo[2.2.1]hept-2-ene (180 mg, 1.9 mmol) in dimethyl ether (65 ml) at  $-35^\circ\text{C}$ . The mixture was stirred for 25 min at  $-28^\circ\text{C}$ , filtered through a precooled silica gel pad (12 cm), and eluted with cold isopentane (70 ml). Evaporation in vacuo at  $-28^\circ\text{C}$  to ca. 5 ml gave a yellow solid. The mother-liquor was removed with a syringe. The solid was washed with cold isopentane (5 ml) and methanol (3 ml), transferred to a Schlenk tube, and dried in vacuo to leave yellow microcrystals or  $\text{Ir}_4(\text{CO})_{11}(\text{C}_7\text{H}_{10})$  (238 mg, 74%).

Found: C, 18.4; H, 0.83.  $C_{18}H_{10}O_{11}Ir_4$  calcd.: C, 18.4; H, 0.86%. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  2096m, 2062vs, 2023vs, 1849m, 1828m. V is thermally unstable and must be stored under nitrogen at  $-20^\circ C$ . It slowly decompose in  $CHCl_3$  or  $CH_2Cl_2$  above  $-20^\circ C$  giving  $Ir_4(CO)_{12}$  and an unidentified green-brown product.

*Undecacarbonyl(5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene)tetrairidium (IV)*. The procedure used for V, but starting with I (503 mg, 0.39 mmol) in dimethyl ether (100 ml), a six-fold excess of ligand and a stoichiometric amount of  $AgBF_4$  (80 mg, 0.41 mmol), culminating in recrystallization from  $Me_2O/MeOH$  gave yellow microcrystals of  $Ir_4(CO)_{11}(C_8H_8O)$  (332 mg, 71%). Found: C, 19.5; H, 0.70.  $C_{19}H_8O_{12}Ir_4$  calcd.: C, 19.1; H, 0.67%. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  2095m, 2061vs, 2038s, 2023s, 1850s br.

*Decacarbonyl(bicyclo[2.2.1]hepta-2,5-diene)tetrairidium (VII)*. A solution of I (505 mg, 0.39 mmol) and nbd (0.5 ml) in  $CH_2Cl_2$  (150 ml) was vigorously stirred after addition of  $AgBF_4$  (100 mg, 0.51 mmol) for 40 min at  $-28^\circ C$ , filtered through a  $20 \times 2$  cm column packed with silica gel (70–230 mesh), and eluted with cold  $CH_2Cl_2$  (80 ml). The yellow filtrate (solution A) was stable at  $-28^\circ C$  for 70 h. Its IR spectrum in  $CH_2Cl_2$  ( $\nu(CO)$  2094m, 2064vs, 2028vs, 1887w, 1845s, 1826s) and  $^1H$  NMR spectrum (Table 1) indicated the presence of  $Ir_4(CO)_{11}(\eta^2\text{-nbd})$  (VI), which could not be isolated as a solid. Solution A was kept at  $30^\circ C$  for 32 h then evaporated under reduced pressure. The resulting yellow-brown oil was extracted with  $CH_2Cl_2$  ( $3 \times 5$  ml), leaving insoluble  $Ir_4(CO)_{12}$  (190 mg; 44%). The extracts were chromatographed on a column ( $80 \times 2$  cm) packed with silica gel (230–400 mesh) with  $CH_2Cl_2$ /pentane (1/5) and yielded yellow crystals of  $Ir_4(CO)_{10}(C_7H_8)$  (VII) (192 mg, 43%). Found: C, 18.0; H, 0.73.  $C_{17}H_8O_{10}Ir_4$  calcd.: C, 17.9; H, 0.70%. IR (cyclohexane):  $\nu(CO)$  2086m, 2069s, 2056vs, 2024s, 2011m, 2002w, 1888w, 1839s, 1823s.  $^1H$  NMR: see Table 3.  $^{13}C$  NMR: see Table 2.

The yield of VII can be increased (55%) by stirring solution A with  $Me_3NO \cdot 2H_2O$  (1.2 equiv.) at  $-28^\circ C$  for 25 h. However, the formed  $Ir_4(CO)_{12}$  is then contaminated by decomposition products and cannot be recycled. No evidence for the formation of  $Ir_4(CO)_8(\text{nbd})_2$  was found when larger amounts of  $Me_3NO \cdot 2H_2O$  were used.

*Decacarbonyl(cycloocta-1,5,-diene)tetrairidium (VIII) and octacarbonylbis(cycloocta-1,5-diene)tetrairidium (IX)*. VIII: The procedure described for VII was used but starting from I and 1,5-cod; yield 45%; IR and  $^{13}C$  NMR: see [10].  $^1H$  NMR: see Table 3.

IX:  $AgClO_4 \cdot H_2O$  (74 mg, 0.33 mmol) was added to a solution of I (322 mg, 0.25 mmol) and 1,5-cod (3 ml) in  $CH_2Cl_2$  (40 ml) at  $-28^\circ C$ . The mixture was stirred for 35 min, filtered through silica gel (20 cm), and washed with  $CH_2Cl_2$  (90 ml).  $Me_3NO \cdot 2H_2O$  (63 mg, 0.57 mmol) was added to the yellow filtrate. The mixture was stirred at  $-28^\circ C$  for 15 h then evaporated to dryness. Chromatography on a  $150 \times 2$  cm column packed with silica gel (320–400 mesh), first with  $CH_2Cl_2$ /pentane (1/8) then with  $CH_2Cl_2$ /pentane (1/3), gave VIII (42 mg, 15%) followed by IX (115 mg, 38%). IR and  $^{13}C$  NMR: see [10].  $^1H$  NMR ( $CD_2Cl_2$ , 190 K):  $\delta$  4.44, 4.31 (2m, 4H, radial HC=C), 3.41, 3.34 (2m, 4H, axial HC=C), 3.06, 2.88 (2m, 4H, outer H(3,8)), 2.57, 2.42 (2m, 4H, outer H(4,7)), 2.13 (m, 4H, inner H(3,8)), 1.86, 1.74 (2m, 4H, inner H(4,7)).

*Decacarbonyl(cyclooctatetraene)tetrairidium (X)*. The procedure described for VII, but starting from I (500 mg, 0.39 mmol), excess cot (3 ml), and  $AgBF_4$  (86 mg, 0.44 mmol) in  $CH_2Cl_2$  (180 ml) culminating in recrystallization from  $CH_2Cl_2$ /methanol



at  $-25^{\circ}\text{C}$  gave  $\text{Ir}_4(\text{CO})_{10}(\text{C}_8\text{H}_8)$  (91 mg, 20%). Treating the solution, after removal of AgBr by filtration, with 1.5 equiv. of  $\text{Me}_3\text{NO}$  gave only lower yields of X. Found: C, 18.9; H, 0.81.  $\text{C}_{18}\text{H}_8\text{O}_{10}\text{Ir}_4$  calcd.: C, 18.7; H, 0.70%. IR (cyclohexane):  $\nu(\text{CO})$  2089m, 2069m, 2060vs, 2038m, 2026s, 2015m, 2006m, 1849m, 1841m.

*Reactions of the olefin complexes with CO.* A slow stream of carbon monoxide was passed through a  $\text{CH}_2\text{Cl}_2$  solution (10 ml) containing 0.05–0.1 g of complex. The initial yellow colour rapidly disappeared, and after 30 min (for II–V) or 2 h (for VII–X),  $\text{Ir}_4(\text{CO})_{12}$  was isolated in quantitative yield.

*Reaction of the olefin complexes with  $\text{SO}_2$ .* An excess of  $\text{SO}_2$  was bubbled through a solution of II–V (ca. 50 mg) in  $\text{CH}_2\text{Cl}_2$  (5 ml) at  $-10^{\circ}\text{C}$ . After stirring for 15 min at room temperature, concentration of the solution and addition of n-hexane precipitated the yellow microcrystalline  $\text{Ir}_4(\text{CO})_{11}(\text{SO}_2)$  [19] ( $\geq 90\%$  yield).

In contrast to the behaviour of the mono-olefin complexes, exposure of a stirred solution of VII, VIII or IX in  $\text{CH}_2\text{Cl}_2$  to a large excess of  $\text{SO}_2$  during 40 h did not result in the displacement of the diolefin, and the complexes were recovered quantitatively.

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