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The use of half-sandwich iridium dithiolate and diselenolate complexes, Cp*Ir(L)(ER)$_2$ (L = CO, PMe$_3$, PPh$_3$; ER = SPh, SePh, SeMe), for the synthesis of heterodimetallic compounds. The molecular structure of Cp*Ir(CO)(μ-SePh)$_2$[Mo(CO)$_4$][1]

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Abstract

Carbonyl–iridium half-sandwich compounds, Cp*Ir(CO)(EPh)$_2$ (E = S, Se), were prepared by the photo-induced reaction of Cp*Ir(CO)$_2$ with the diphenyl dichalcogenides, E$_2$Ph$_2$, and used as neutral chelating ligands in carbonylmetal complexes such as Cp*Ir(CO)(μ-EPh)$_2$[Cr(CO)$_4$], Cp*Ir(CO)(μ-EPh)$_2$[Mo(CO)$_4$] and Cp*Ir(CO)(μ-EPh)$_2$[Fe(CO)$_3$], respectively. A trimethylphosphane–iridium analogue, Cp*Ir(PMe$_3$)(μ-SeMe)$_2$[Cr(CO)$_4$], was also obtained. The new heterodimetallic complexes were characterized by IR and NMR spectroscopy, and the molecular geometry of Cp*Ir(CO)(μ-SePh)$_2$[Mo(CO)$_4$] has been determined by a single crystal X-ray structure analysis. According to the long Ir...Mo distance (395.3(1) Å), direct metal–metal interactions appear to be absent. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Half-sandwich iridium complexes; Heterodimetal complexes; Chromium; Molybdenum; Iron; NMR spectra; Crystal structure

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1. Introduction

Homodinuclear pentamethylcyclopentadienyl iridium (Cp*Ir) complexes containing sulfur and selenium bridges—e.g. [Cp*Ir(L)(μ-E)]$_2$ (L = CO, E = S [1,2], Se [1]; L = ^{t}BuN≡C, E = S [2]), Cp*Ir(PMe$_3$)(μ-S)$_2$Ir(L)Cp* (L = CO [2], ^{t}BuN≡C [2]), Cp*(PMe$_3$)Ir(μ-S)$_2$IrCp* [2] and Cp*Ir(μ-Se)(μ-Se$_4$)IrCp* [1]—are well-known, and pseudocubane tetramers, [Cp*Ir(μ-E)]$_4$ (E = S [1–3], Se [1,4], Te [4]), have been structurally characterized. Tri- and tetranuclear cations such as [Cp$^*_3$Ir$_3$(μ_3-S)$_2$]$^{2+}$ and [Cp$^*_4$Ir$_4$(μ_3-S)$_4$]$^{2+}$ have also been described [3]. The intermediate formation of a coordinatively unsaturated dimer, {Cp*Ir(μ-S)}$_2$, has occasionally been postulated [2,3].

In the light of the nucleophilic behaviour of chalcogen ligands and the easy formation of μ_2-chalcogen bridges in binuclear iridium complexes, it is not surprising that bis(chalcogenato) iridium compounds of the type Cp*Ir(L)(ER)$_2$ (E = S, Se) are able to act as bidentate ligands through their chalcogen atoms. These bis(chalcogenato)iridium educts are accessible either from the iridium(I) dicarbonyl, Cp*Ir(CO)$_2$ (**1**), or from the iridium(III) dihalides, Cp*Ir(L)Cl$_2$ (L = PMe$_3$ (**2**), PPh$_3$ (**3**)).

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[1] Dedicated to Professor Bernt Krebs, Münster, on the occasion of his 60th birthday.

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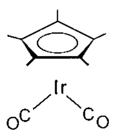

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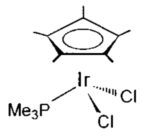

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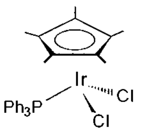

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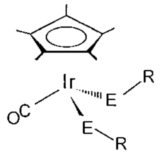
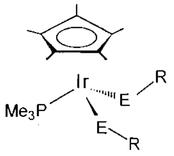
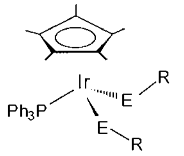


4a : ER = SPh
4b : ER = SePh
4b' : ER = SeMe



5a : ER = SPh
5b : ER = SePh
5b' : ER = SeMe



6a : ER = SPh
6b : ER = SePh

2. Results and discussion

2.1. Syntheses

Irradiation of $Cp^*Ir(CO)_2$ (**1**) in THF solution in the presence of disulfides or diselenides, E_2R_2, leads to the monocarbonyls **4a,b,b′** under formal oxidation of iridium(I) to iridium(III), (Eq. 1):

$$Cp^*Ir(CO)_2\ (\mathbf{1}) + E_2R_2 \xrightarrow[(THF)]{h\nu,\ -CO} Cp^*Ir(CO)(ER)_2 \qquad (1)$$

ER = SPh (**4a**), SePh (**4b**), SeMe (**4b′**)

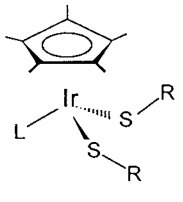
The yields of **4a,b,b′** after column chromatography and recrystallization are in the range of 85–95%. Subsequent displacement of the remaining carbonyl ligand by excess trimethylphosphane gives **5a,b,b′** in good yields.

The triphenylphosphane complexes $Cp^*Ir(PPh_3)(EPh)_2$ (**6a,b**) were prepared by substitution of chloro ligands according to Eq. 2:

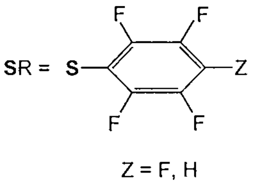
$$Cp^*Ir(PPh_3)Cl_2\ (\mathbf{3}) + 2\ LiEPh \xrightarrow[THF]{-2\ LiCl} Cp^*Ir(PPh_3)(EPh)_2 \qquad (2)$$

E = S (**6a**), Se (**6b**)

The analogous reaction of **2** with NaSR in ethanol had been used by Bergman and co-workers [5] to prepare the related trimethylphosphane complexes $Cp^*Ir(PMe_3)(SR)_2$ (R = H, Me, ^{t}Bu). On the other hand, the coordinatively unsaturated pentafluorthiolato- and 2,3,5,6-tetrafluorthiolato complexes, $Cp^*Ir(SC_6F_5)_2$ and $Cp^*Ir(S\text{-}C_6F_4\text{-}H(p))_2$ [6], were reported to add carbon monoxide and triphenylphosphane, respectively, to give complexes of type **7a** and **8a** [7], which are analogous to **4a** and **6a**.

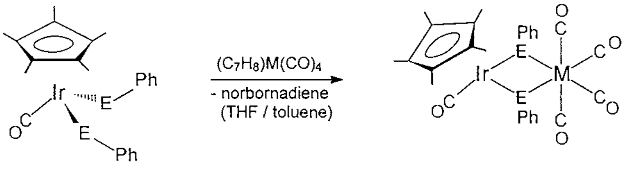


L = CO (**7a**)
PMe3 (**8a**)



Z = F, H

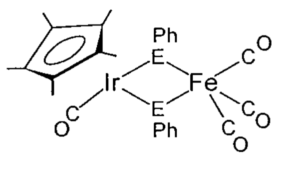
The carbonyliridium compounds $Cp^*Ir(CO)(EPh)_2$ (**4a,b**) react with the norbornadiene-stabilised tetracarbonylmetal fragments, $M(CO)_4(nor\text{-}C_7H_8)$ (M = Cr, Mo), to give the heterodimetallic complexes $Cp^*Ir(CO)(\mu\text{-}EPh)_2[M(CO)_4]$ (**9a,b** and **10a,b**) in which the phenylchalcogenido ligands assume a bridging function:



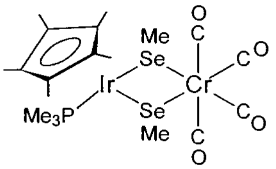
E = S (**4a**)
Se (**4b**)

E = S; M = Cr (**9a**), Mo (**10a**)
Se; M = Cr (**9b**), Mo (**10b**)

Related tricarbonyliron complexes **11a,b** are obtained by a photo-induced reaction of $Cp^*Ir(CO)(EPh)_2$ (E = S (**4a**), Se (**4b**)) with $Fe(CO)_5$. The solubility of the molybdenum- and iron heterodimetal complexes is low, also in polar solvents such as THF and acetonitrile.



E = S (**11a**)
Se (**11b**)



12b'

In contrast to the carbonyl–iridium complexes **4a,b**, the triphenylphosphane–iridium compounds **6a,b** did not add tetracarbonylmetal fragments such as $[Cr(CO)_4]$ and $[Mo(CO)_4]$ under comparable conditions. Some reactions with the trimethylphosphane complex, $Cp^*Ir(PMe_3)(SeMe)_2$ (**5b′**), have also been carried out, and a heterodinuclear derivative, $Cp^*Ir(PMe_3)(\mu\text{-}SeMe)_2[Cr(CO)_4]$ (**12b′**), has been characterized. Preliminary studies of the reaction between **5b′** and bis(cycloocta-1,5-diene)nickel indicated the formation of a red, paramagnetic product of the composition $[Cp^*Ir(SeMe)_3]_2Ni$ (**13**).

2.2. Spectroscopic characterization

The relevant spectroscopic data of the mononuclear Cp*Ir complexes are collected in Table 1, those of typical heterobimetallic derivatives in Table 2.

In the IR spectra, the $Cp^*Ir(CO)(ER)_2$ compounds (**4a,b,b′**) each contain a strong carbonyl absorption (Ir–CO) close to 2000 cm^{-1} which appears with roughly the same frequency (1995–2011 cm^{-1}) in the heterobimetallic complexes (Table 2). The number of carbonyl bands equals the total number of CO ligands. All IR spectra contain the strong Cp* absorption at 1375 ± 3 cm^{-1} which is ascribed to the out-of-plane vibrations ($\gamma(CH_3)$) of the methyl substituents.

Table 1
IR- and NMR spectroscopic data[a] of the mononuclear Cp*Ir complexes

Complex		IR (CsI) ν(CO) [cm^{-1}]	^{1}H-NMR[b]		^{13}C-NMR	^{31}P-NMR
4a	Cp*Ir(CO)(SPh)$_2$	1994	1.73s	(15)	8.6; 101.4 (Cp*)	
			6.99m, 7.38m	(10)	123.9, 127.6, 132.2 (Ph)	
					141.4 (C^i)	
					171.2 (CO)	
4b	Cp*Ir(CO)(SePh)$_2$	1994	1.77s	(15)	8.9; 100.3 (Cp*)	
			7.05m, 7.56m	(10)	125.1, 127.8, 134.6 (Ph)	
					137.1 (C^i)	
					170.8 (CO)	
4b′	Cp*Ir(CO)(SeMe)$_2$	1999	1.96s	(15)	9.1; 99.8 (Cp*)	
			1.88s	(6)	−1.1 (SeMe)	
					174.4 (CO)	
5a	Cp*Ir(CO)(PMe$_3$)(SPh)$_2$		14.7d [1.8]	(15)	9.3s, 94.9d [3.2] (Cp*)	−40.6
			1.53d [10.8]	(9)	12.3d [40.5] (PMe$_3$)	
			6.92 m, 7.37m	(10)	122.2, 127.8, 132.0 (Ph)	
					140.8 (C^i)	
5b	Cp*Ir(PMe$_3$)(SePh)$_2$		1.78d [2.7]	(15)	9.5s; 94.3d [3.4] (Cp*)	−43.8
			1.62d [9.9]	(9)	16.3d [40.5] (PMe$_3$)	
			6.96m,7.48m	(10)	123.8; 127.2; 134.9 (Ph)	
					132.8d [5.9] (C^i)	
5b′	Cp*Ir(PMe$_3$)(SeMe)$_2$		1.74d [2.0]	(15)	9.1s; 93.6d [3.4] (Cp*)	−39.9
			1.53d [8.6]	(9)	16.6d [41.0] (PMe$_3$)	
			1.68s	(6)	−5.2s (SMe)	
6a	Cp*Ir(PPh$_3$)(SPh)$_2$		1.46d [2.2]	(15)	8.6s; 96.3d [3.4] (Cp*)	−4.0
			6.75m, 6.91m		122.8, 126.5, 133.9 (SPh)	
			7.30m	(25)	141.2d [4.3] (C^i)	
					127.3, 127.6, 129.9 (PPh$_3$)	
					134.9d [7.7] (C^i)	
6b	Cp*Ir(PPh$_3$)(SePh)$_2$		1.52d [2.7]	(15)	9.1s; 95.8d [2.5] (Cp*)	−3.0
			6.86m, 7.25m	(25)	124.5, 126.9, 136.3 (SePh)	
					131.8 (C^i)	
					127.2, 127.6, 129.9 (PPh$_3$)	
					134.9d [7.7] (C^i)	

[a] All NMR spectra were measured in CDCl$_3$ solution at r.t. Coupling constants $^nJ(^{31}P, ^1H)$ and $^nJ(^{31}P, ^{13}C)$ are given in square brackets.

[b] Relative intensities in parentheses.

The Cp* ring ligands are easily recognized both in the ^{1}H- and ^{13}C-NMR spectra by the intense signals of their methyl substituents. The methyl proton signal is split into a doublet in the phosphane-containing compounds by ^{31}P–^{1}H spin-spin coupling ($^4J(P,H) = 2–3$ Hz), whereas the ^{13}C-NMR methyl signal always appears as a singlet (Table 1 and Table 2).

The electron impact (EI) mass spectra (see Section 3) of the mononuclear carbonyl (**4a,b,b′**) and trimethylphosphane (**5a,b,b′**) compounds contain the molecular ion (M$^+$), whereas the heterodimetallic complexes only show CO-deficient species in the higher mass region.

*2.3. Molecular structure of Cp*Ir(CO)(μ-SePh)$_2$[Mo(CO)$_4$] (**10b**)*

The bond distances and angles related to the coordination spheres of both iridium(III) and molybdenum(0) are given in Table 3, cf. Fig. 1.

The central four-membered ring connecting the two metals via selenolate bridges is almost planar. The long distance Ir...Mo (395.3(1) Å) and the obtuse angles Ir–Se–Mo (98.8(1)°) indicate that direct bonding interactions between the two metals are absent. The bond distance of the selenolate ligands to their central metal iridium(III) (250.3(1) Å) are distinctly shorter than the corresponding distances to the attached molybdenum(0) unit (270.3(2) Å). It is therefore fitting to consider the Cp*Ir(CO)(SePh)$_2$ molecule as a neutral chelate ligand which has formally replaced two *cis*-carbonyl groups in the Mo(CO)$_6$ octahedron.

3. Experimental

All manipulations were routinely carried out under argon using Schlenk techniques. The solvents (hexane, THF) were heated under reflux over an Na/K alloy and then distilled off in a stream of argon. Separation of

Table 2
IR- and NMR spectroscopic data[a] of the heterodimetallic complexes

Complex		IR (CsI) ν(CO)[cm^{-1}]	^{1}H-NMR[b]		^{13}C-NMR
9a	$Cp^*Ir(CO)(SPh)_2[Cr(CO)_4]$	2004[c]	1.97s	(15)	9.1s; 102.0s (Cp*)
		2042, 1893	7.13m, 7.44m		126.1, 128.5, 131.1 (Ph)
		1869, 1816		(10)	142.0 (C^i)
					211.3 (CO)
9b	$Cp^*Ir(CO)(SePh)_2[Cr(CO)_4]$	1995[c]	2.03s	(15)	
		2030, 1898	7.16m, 7.59m		
		1869, 1834		(10)	
10a	$Cp^*Ir(CO)(SPh)_2[Mo(CO)_4]$	2011[c]	1.98s	(15)	9.1s; 102.3s (Cp*)
		2047, 1897	7.13m, 7.46m		126.1, 128.2, 131.1 (Ph)
		1870, 1827		(10)	131.6 (C^i)
10b	$Cp^*Ir(CO)(SePh)_2[Mo(CO)_4]$	2009[c]	2.03s	(15)	
		2031, 1909	7.16m, 7.59m		
		1870, 1840		(10)	
11b	$Cp^*Ir(CO)(SePh)_2[Fe(CO)_3]$	1997[c]	2.21s	(15)	
		2064	7.18m, 7.34m		
		2031, 1980		(10)	
12b′	$Cp^*Ir(PMe_3)(SeMe)_2[Cr(CO)_4]$[d]	1983, 1873	1.73d [2.5]	(15)	9.4s; 94.9s (Cp*)
		1855, 1815	1.89d [9.8]	(9)	1.67d [40.5] (PMe_3)
			1.64s	(6)	0.68s (SeMe)

[a] All NMR measurements were carried out in $CDCl_3$ at r.t. Coupling constants $J(^{31}P, ^1H)$ and $J(^{31}P, ^{13}C)$ are given in square brackets. [b] Relative intensities in parentheses. [c] Carbonyl ligand at iridium. [d] ^{31}P-NMR: $\delta = -28.4$.

product mixtures and purification of the components was accomplished by column chromatography over silica (Merck, Kieselgel 60, 0.06–0.2 mm) which had been activated at 600°C over night and then kept under argon before use.

The starting materials $Cp^*Ir(CO)_2$ (**1**) [8], $Cp^*Ir(PMe_3)Cl_2$ (**2**) [8], $Cp^*Ir(PPh_3)Cl_2$ (**3**) [9], and (nor–C_7H_8)$M(CO)_4$ (M = Cr, Mo [10]) were prepared following established procedures.

The standard ^{1}H- and ^{13}C-NMR spectra were recorded on a Jeol FX 90Q instrument ($CDCl_3$, 0°C) using the $CHCl_3$ trace as a reference. The IR spectra were measured on a Perkin-Elmer 983G (as CsI pellets), and the electron-impact mass spectra on a Varian MAT 8500 spectrometer (70 eV).

Table 3
Selected bond distances and angles for $Cp^*Ir(CO)(\mu\text{-}SePh)_2[Mo(CO)_4]$ (**10b**)

Bond distances (Å)			
Ir–C(1)	186(1)	Mo–C(2)	202(1)
Ir–Center(Cp*)	186.6(9)	Mo–C(3)	195(1)
Ir–Se(1)	250.3(1)	Mo–C(4)	189(1)
Ir–Se(2)	250.2(1)	Mo–C(5)	204(1)
Ir...Mo	395.3(1)	Mo–Se(1)	270.4(2)
		Mo–Se(2)	270.2(2)
Bond angles (°)			
Center(Cp*)–IrC(1)	132.2(5)	Se(1)–Mo–C(2)	97.7(4)
Center(Cp*)–Ir–Se(1)	124.0(5)	Se(1)–Mo–C(3)	98.4(4)
Center(Cp*)–Ir–Se(2)	124.2(5)	Se(1)–Mo–C(4)	173.5(4)
C(1)–Ir–Se(1)	89.0(4)	Se(1)–Mo–C(5)	88.1(4)
C(1)–Ir–Se(2)	90.6(4)	C(2)–Mo–C(3)	91.2(5)
Se(1)–Ir–Se(2)	82.1(1)	C(2)–Mo–C(4)	87.4(5)
Ir–Se(1)–Mo	98.7(1)	C(2)–Mo–C(5)	174.1(5)
Ir–Se(2)–Mo	98.8(1)	C(3)–Mo–C(4)	85.5(6)
Se(1)–Mo–Se(2)	74.9(1)	C(3)–Mo–C(5)	89.1(5)
		C(4)–Mo–C(5)	86.8(6)

*3.1. Preparation of the Cp*Ir half-sandwich complexes*

3.1.1. Synthesis of carbonyl–iridium complexes, $Cp^*Ir(CO)(ER)_2$ (4a,b,b′)

$Cp^*Ir(CO)(SePh)_2$ (**4b**): A yellow solution containing 0.25 g (0.65 mmol) $Cp^*Ir(CO)_2$ (**1**) and 0.20 g (0.65

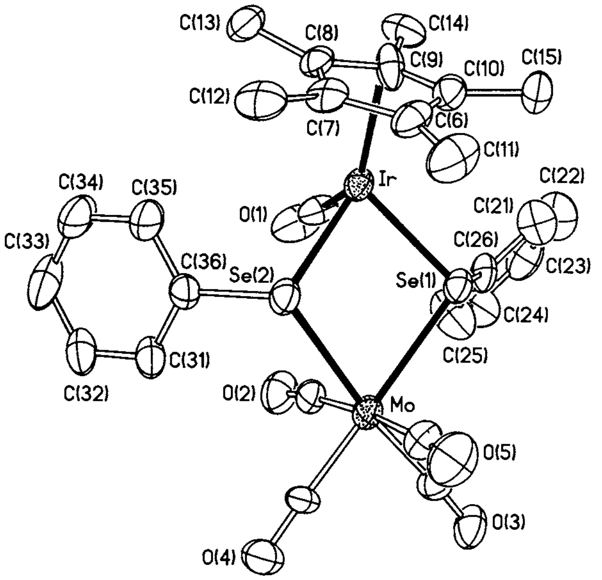


Fig. 1. Molecular structure of $Cp^*Ir(CO)(\mu\text{-}SePh)_2[Mo(CO)_4]$ (**10b**)

mmol) Se_2Ph_2 in 60 ml of THF was irradiated for 40 min at 15°C. The colour changed gradually from yellow to red while gas (CO) was liberated. The solvent THF was evaporated in vacuo and the residue chromatographed on a silica column. Elution with CH_2Cl_2/pentane (1:1) gave a red zone of **4b**, and recrystallization from $CHCl_3$/hexane at −25°C produced 0.42 g (97%) of red needles (m.p. 152°C). The complex **4b** is soluble in polar solvents such as CH_2Cl_2, $CHCl_3$, Et_2O, THF, acetone and acetonitrile, but almost insoluble in saturated hydrocarbons. EI-MS: m/e ($I_{rel.}$, %) 668 (M^+, 10%), 640 (M^+–CO, 5%), 588 (M^+–Se, 3%), 513 ($Cp^*Ir(CO)Se_2^+$, 39%), 486 ($Cp^*IrSe_2^+$, 100%), 403 (Cp^*IrSe^+, 24%). Analogous procedures were used to prepare **4a** and **4b′**.

$Cp^*Ir(CO)(SPh)_2$ (**4a**): orange–yellow prismatic crystals, m.p. 147°C (yield 88%). EI-MS: m/e ($I_{rel.}$) 574 (M^+, 6%), 546 (M^+–CO, 10%), 465 (M^+–PhS, 22%), 437 ($Cp^*Ir(SPh)^+$, 100%), 360 (Cp^*IrS^+, 9%).

$Cp^*Ir(CO)(SeMe)_2$ (**4b′**): orange–golden plates, m.p. 124°C, (yield 95%). EI-MS: m/e 544 (M^+, 45%), 516 (M^+–CO, 4%), 504 (M^+–CO–Me, 34%), 486 ($Cp^*IrSe_2^+$, 70%), 451 (M^+–SeMe, 84%), 421 ($Cp^*Ir(SeMe)^+$, 100%).

*3.1.2. Synthesis of trimethylphosphane–iridium complexes, $Cp^*Ir(PMe_3)(ER)_2$ (**5a,b,b′**)*

$Cp^*Ir(PMe_3)(SPh)_2$ (**5a**): A yellow THF solution (50 ml) of 0.20 g (0.35 mmol) $Cp^*Ir(CO)(SPh)_2$ (**4a**) was irradiated in the presence of 0.09 ml (1 mmol) PMe_3. After 20 min the ν(CO) stretching absorption had vanished. The solvent was removed under reduced pressure and the residue chromatographed on a silica column. A red zone of **5a** was eluted using CH_2Cl_2 from which prismatic orange crystals (m.p. 137–138°C) were obtained by crystallization from toluene/hexane at −78°C. Yield 0.19 g (87.6%). EI-MS: m/e ($I_{rel.}$) 622 (M^+, 11%), 546 (M^+–PMe_3, 8%), 513 (M^+–SPh, 100%), 437 ($Cp^*Ir(SPh)^+$, 74%).

In a similar manner **4b** and **4b′** were photo-decarbonylated in the presence of a 3-fold molar excess of PMe_3 in THF solution to give **5b** and **5b′**.

$Cp^*Ir(PMe_3)(SePh)_2$ (**5b**), red prisms m.p. 140–141°C, yield 95%. EI-MS: m/e ($I_{rel.}$) 716 (M^+, 8%), 640 (M^+–PMe_3, 5%), 563 (M^+–PMe_3–Ph, 24%), 559 (M^+–SePh, 100%), 583 ($Cp^*Ir(SePh)^+$, 60%).

$Cp^*Ir(PMe_3)(SeMe)_2$ (**5b′**) orange–red prisms, m.p. 215°C, yield 94%. EI-MS: m/e ($I_{rel.}$) 592 (M^+, 10%), 577 (M^+–Me, 2%), 516 (M^+–PMe_3, 1%), 497 (M^+–SeMe, 100%), 482 ($Cp^*Ir(PMe_3)Se^+$, 24%).

*3.1.3. Synthesis of triphenylphosphane–iridium complexes, $Cp^*Ir(PPh_3)(EPh)_2$ (**6a**, **6b**)*

A solution of 0.30 mmol S_2Ph_2 or Se_2Ph_2 in 10 ml THF was treated with 0.60 ml (0.60 mmol) ‘superhydride’, $LiBHEt_3$, and stirred for 30 min at room temperature (r.t.). A solution of 0.20 g (0.30 mmol) $Cp^*Ir(PPh_3)Cl_2$ in 40 ml of THF was added. The reaction mixture was stirred for 1 h and then filtered. The red filtrate was concentrated under vacuum and transferred to the top of a chromatography column containing silica. Elution with CH_2Cl_2/pentane (2:1) and workup of the red zone gave red crystals which were recrystallized from $CHCl_3$/hexane (−25°C).

$Cp^*Ir(PPh_3)(SPh)_2$ (**6a**), m.p. 160–161° (dec.), yield 0.22 g (90.8%). EI-MS: m/e ($I_{rel.}$) 546 (M^+–PPh_3, 22%), 514 (M^+–PPh_3–S, 2%), 469 (M^+–PPh3–Ph, 5%), 437 ($Cp^*Ir(SPh)$, 100%), 360 ($Cp^*Ir(S)^+$, 6%).

$Cp^*Ir(PPh_3)(SePh)_2$ (**6b**), m.p. 163–164°C, yield 0.25 g (92.4%). EI-MS: m/e ($I_{rel.}$) 640 (M^+–PPh_3, 18%), 562 (M^+–PPh_3–Se, 78%), 485 ($Cp^*Ir(SePh)^+$, 45%), 482 $Cp^*Ir(Se_2)^+$, 42%.

3.2. Preparation of heterodimetallic complexes

3.2.1. General procedure

A solution containing 0.3–0.5 mmol of the ligand $Cp^*Ir(CO)(EPh)_2$ ($E = S$ (**4a**), Se (**4b**)) and an equimolar amount (0.3–0.5) of the η^4-norbornadiene complex, $M(CO)_4(nor–C_7H_8)$ ($M = Cr$, Mo), in 50 ml of a toluene/THF (1:1) mixture was stirred for 2–4 h at ambient temperature. The colour of the solution became intensely dark-red or brown. Evaporation of the solvents and purification of the residue by column chromatography on silica (elution with CH_2Cl_2 (**9a,b**) or CH_2Cl_2/THF (**10a,b**; **12b′**)) gave a red–brown zone containing the desired product which was recrystallized from chloroform/hexane mixtures.

$Cp^*Ir(CO)(SPh)_2[Cr(CO)_4]$ (**9a**): yield 0.28 g (90.7%), dark–brown needles, m.p.166–168° (dec.). EI-MS: m/e ($I_{rel.}$), M^+ not observed, 684 (M^+–2CO, 0.5%), 656 (M–3CO, 4%), 628 (M^+–4CO, 5%), 384 ($Cr(CO)_4(SHPh)_2^+$, 68%), 352 ($Cr(CO)_4SPh_2H^+$, 100%).

$Cp^*Ir(CO)(SePh)_2[Cr(CO)_4]$ (**9b**): yield 80.3%, dark-red crystals, m.p.177–178° (dec.). EI-MS: m/e ($I_{rel.}$) 720 (M^+–4CO, 3%), 692 (M^+–5CO, 5%), 614 (M^+–5CO–Se, 5%), 538 ($Cp^*Ir(Se_2)Cr^+$, 14%), 534 ($Cp^*IrPh_2Cr^+$, 10%), 482 ($Cp^*IrPh_2^+$, 100%), 405 (Cp^*IrPh^+, 100%).

$Cp^*Ir(CO)(SePh)_2[Mo(CO)_4]$ (**10b**): yield 84%, dark-red prismatic crystals, m.p.191–192° (dec.). IR (CsI): ν(CO) 2031, 1909, 1870, 1840 [$Mo(CO)_4$] and 2009 (Ir–CO) cm^{-1}. The crystalline tetracarbonylmolybdenum complexes **10a,b** are only slightly soluble even in polar solvents such as THF, acetone and acetonitrile.

Crystals suitable for an X-ray structure determination were grown at the interface between the solution of **4b** in THF and the solution of $Mo(CO)_4(nor–C_7H_8)$ in toluene.

$Cp^*Ir(CO)(SePh)_2[Fe(CO)_3]$ (**11b**): An orange solution containing 0.32 g (0.48 mmol) $Cp^*Ir(CO)(SePh)_2$

(**4b**) and 0.4 ml (3.04 mmol) $Fe(CO)_5$ in 40 ml of THF was irradiated for 20 min. Gas evolution (CO) was observed, and the colour of the solution turned dark-red. The solvent was evaporated and the residue chromatographed on silica, using a CH_2Cl_2/pentane (1:1) mixture for elusion. A dark-red zone was obtained which contained 0.28 g (72.4%) **11b**. Recrystallization from $CHCl_3$/hexane at −25° afforded dark-red crystals, m.p. 140–142° (dec.). EI-MS: *m*/*e* ($I_{rel.}$) 752 (M^+−2CO, 0.2%), 696 (M^+−4CO, 0.4%), 538 ($Cp^*Ir(SePh)Fe^+$, 18%), 424 ($Fe_2(SePh)_2^+$, 100%).

$Cp^*Ir(PMe_3)(SeMe)_2[Cr(CO)_4]$ (**12b′**): The reaction of equimolar amounts of **5b** and $Cr(CO)_4(nor{-}C_7H_8)$ in toluene/THF (1:1) gave black prismatic crystals in 64% yield, m.p. 198°C. EI-MS: *m*/*e* ($I_{rel.}$) 728 (M^+−CO, 6%), 672 (M^+−3CO, 8%), 644 (M^+−4CO 15%), 629 (M^+−4CO−Me, 14%), 614 (M^+−4CO−2Me, 15%), 538 ($Cp^*IrSe_2Cr^+$, 40%), 512 ($Cp^*Ir(PMe_3)SeMe_2^+$, 4%), 497 ($Cp^*Ir(PMe_3)SeMe^+$, 40%), 432 ($Cp^*Ir(PMe_3)Me_2^+$, 100%).

$[Cp^*Ir(SeMe)_3]_2Ni$ (**13**): The solution of 0.19 g (0.70 mmol) $Ni(C_8H_{12})_2$ in 10 ml of THF was slowly added at −78°C to a solution containing 0.66 g (1.10 mmol) $Cp^*Ir(CO)(SeMe)_2$ (**4b′**) in 80 ml of THF. The colour changed immediately from orange to violet. The mixture was kept at −78°C for 0.5 h. During this time two ν(CO) absorptions (at 2007 and 1935 cm^{-1}) could be observed if the spectra were measured quickly. The mixture was then allowed to reach r.t. and stirred for additional 2 h. The solvent was evaporated and the residue given on a chromatography column filled with silica. Elution with CH_2Cl_2 developed a red zone which contained 0.24 g (34%) of the product **13** which was recrystallized from $CHCl_3$/hexane at −25°C. Calc. for $C_{26}H_{48}Ir_2NiSe_6$ (1277.56): C 24.44, H 3.78, Ir 30.09, Se 37.08%. Found: C 24.42, H 3.74, Ir 29.8, Se 36.4%. FD-MS: *m*/*e* 1277.7, correct isotope pattern. IR: 1377 (δ(Cp*)), 1278 cm^{-1} ($\delta(SeCH_3)$).

3.3. X-ray structure determination of $Cp^*Ir(CO)(\mu\text{-}SePh)_2[Mo(CO)_4]$ (10b)

Crystal: $C_{27}H_{25}IrMoO_5Se_2$, red, with the dimensions $0.18 \times 0.26 \times 0.36$ mm^3. Space group $P2_1/n$ (monoclinic) with the lattice parameters $a = 1346.6(3)$, $b = 1202.2(2)$, $c = 1735.7(4)$ Å and, $\beta = 91.57(2)°$; $V = 2808.8(6) \times 106$ Å^3, $Z = 4$. $D_{calc.}$ 2.07 g × cm^{-3}; $\mu(Mo{-}K_\alpha)$ 82.8, Transmission [*T*(max.)/*T*(min.)] 0.082/0.035.

Data collection: Nicolet R3, Mo−K_α radiation ($\lambda = 71.073$ Å), graphite monochromator, $T = 292$ K. 2θ scan range 4–54°. Data collected (*h*, *k*, *l*) ± 18, + 16, + 22. Collected reflections 6086, of which 5624 were independent and 3508 independent observed ($F_o > n\sigma(F_o)$, $n = 5$). Control by three standard per 197 reflections, variation in standards ± 1%. Refinement: *R*(*F*) 5.08%, *R*(*wF*) 5.33%, $\Delta\sigma$/(max.) 0.102, $\Delta(\rho)$ 1.23×10^{-6} e Å^3. N_o/N_v 11.6; GOF 1.35.

4. Supplementary data

Tables of all bond distances and bond angles, anisotropic thermal parameters, positional parameters of the hydrogen atoms, and the lists of the observed and calculated structure factors are deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein–Leopoldshafen, under the registry number CSD-59460.

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