# Synthesis and Reactions of the Carbene Complexes $[M(SnPh_3)(CO)_2 = C(OEt)PhL] (M = Mo \text{ or } W; L = \eta - C_5H_5, \eta - C_5Me_5 \text{ or indenyl}, [M(SnPh_3)(CO)_2 = C(OEt)Me](\eta - C_5H_5)] (M = Mo \text{ or } W) \text{ and } [MI(CO)_2 = C(OEt)R](\eta - C_5H_5)] (M = Mo \text{ or } W, R = Me \text{ or } Ph). X-Ray Crystal Structures of$ $<math display="block">[Mo(SnPh_3)(CO)_2 = C(OEt)Ph](\eta - C_5Me_5)] \text{ and } [WI(CO)_2 = C(OEt)Ph](\eta - C_5H_5)]^{\dagger}$

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Treatment of the tricarbonyls  $[M(SnPh_3)(CO)_3L]$   $[M = Mo \text{ or } W; L = \eta - C_5H_5, \eta - C_5H_5, \sigma \eta^5 - C_9H_7-(indenyl)]$  with LiPh followed by  $[OEt_3][BF_4]$  results in the formation of the carbenes  $[M(SnPh_3)-(CO)_2\{=C(OEt)Ph\}L]$  in good to high yields. Related reactions of  $[M(SnPh_3)(CO)_3(\eta - C_5H_5)]$  but using LiMe afford  $[M(SnPh_3)(CO)_2\{=C(OEt)Me\}(\eta - C_5H_5)]$ . The complex *trans*- $[M(SnPh_3)(CO)_2\{=C(OEt)Ph\}(\eta - C_5Me_5)]$  is monoclinic, a = 14.611(36), b = 16.788(20), c = 16.183(30) Å,  $\beta = 96.08(18)^\circ$ , and R = 0.0888 for 2117 independent reflections. While the  $\eta - C_5H_5$  and indenyl complexes exist as pairs of isomers in solution generated by rotation about the  $M=C_{carbene}$  bond, the  $\eta - C_5H_5$ ] (M = Mo or W) with  $I_2$  results in formation of the iodometal species  $[MI(CO)_2\{=C(OEt)Ph\}(\eta - C_5H_5)]$ . The complex  $[WI(CO)_2\{=C(OEt)Ph\}(\eta - C_5H_5)]$  is monoclinic, a = 9.34(3), b = 13.00(2), c = 13.53(3) Å,  $\beta = 97.8(2)^\circ$ , and R = 0.0812 for 2091 independent reflections. In solution this compound exists as three *trans* isomers and one *cis*. Treatment of  $[M(SnPh_3)(CO)_2\{=C(OEt)Ph\}(\eta - C_5Me_5)]$  with  $I_2$  results in the eventual formation of  $[MOPh(CO)_3(\eta - C_5Me_5)]$  in the molybdenum case and  $[MI_3-(CO)_2(\eta - C_5Me_5)]$  in both cases.

Migrations of hydride to carbene or alkylidene<sup>1,2</sup> are important in the context of C-H bond-forming reactions and in the sense that they represent the reverse of  $\alpha$  elimination.<sup>3</sup> We recently reported the directly observable hydride to carbene migration of [MoH(CO)<sub>2</sub>{=C(CH<sub>2</sub>)<sub>3</sub>NMe}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)], which gives [Mo-(CO)<sub>2</sub>{CH(CH<sub>2</sub>)<sub>3</sub>NMe}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)],<sup>2</sup> and briefly mentioned the migrations displayed by complexes of the type [MH(CO)<sub>2</sub>-{=C(X)Ph}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (X = OEt or NHEt).<sup>4</sup> The synthetic strategy leading to hydride complexes of the type [MH(CO)<sub>2</sub>-(carbene)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] is based on protonation of the anions [Mo(CO)<sub>2</sub>(carbene)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup>. These anions are available by Na(C<sub>10</sub>H<sub>8</sub>) reduction of the corresponding iodometal carbene complexes [MoI(CO)<sub>2</sub>(carbene)( $\eta$ -C<sub>5</sub>H<sub>5</sub>)].<sup>5</sup>

To further our studies on migrations to carbenes in general, we therefore require syntheses of complexes  $[MX(carbene)-L_n](X = halide)$  reducible to anions  $[M(carbene)L_n]^-$ . We present here approaches to molybdenum and tungsten complexes of the type  $[MI(CO)_2{=C(OEt)R}(\eta-C_5H_5)]$  (M = Mo or W, R = Me or Ph) and some related systems. Part of this work was the subject of a preliminary communication.<sup>6</sup>

# **Results and Discussion**

Routes to the Carbene Complexes [MI(CO)<sub>2</sub>{=C(OEt)Ph}(η-

 $C_5H_5$ ].—At first sight one might expect that a standard Fischer-carbene type synthesis [(*i*) LiR (R = Me or Ph), (*ii*) Et<sub>3</sub>O<sup>+</sup>] using [MI(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (M = Mo or W) would lead to formation of the complexes [MI(CO)<sub>2</sub>{=C(OEt)R}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] via the anionic acyl [MI(COR)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup>. In practice, this approach fails as a consequence of the iodo ligand. For instance, the major organometallic product of the reaction between [WI(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] and LiR (R = Me or Ph) is the anion [W(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> rather than the desired acyl [WI(COR)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup>.

We have successfully used the reactions of I<sup>-</sup> with alkyls of the type  $[MR(CO)_3(\eta-C_5H_5)]$  (M = Mo or W) to form carbene complexes<sup>7</sup> via intermediate anionic acyl complexes. However the position of the equilibrium between I<sup>-</sup> and  $[WMe(CO)_3(\eta-C_5H_5)]$  is such that the direct reaction between these two species as a route to the formation of  $[WI(COMe)-(CO)_2(\eta-C_5H_5)]^-$  fails. In fact we have already synthesised the acyl anion  $[WI(COMe)(CO)_2(\eta-C_5H_5)]^-$  by another route, but this synthesis is based on the consecutive reactions of  $[WMe(CO)_3(\eta-C_5H_5)]$  with Li(BEt<sub>3</sub>H) and CHI<sub>3</sub> and is not particularly convenient for large-scale work.<sup>8</sup>

Since no very convenient route to acyl anions of the type  $[MI(COR)(CO)_2(\eta-C_5H_5)]^-$  (M = Mo or W, R = Ph or Me) exists, other routes to the carbenes  $[MI(CO)_2\{=C(OEt)R\}(\eta-C_5H_5)]$  are required. We show here that the reaction of complexes of the type  $[M(SnPh_3)(CO)_2\{=C(OEt)R\}(\eta-C_5H_5)]$  (M = Mo or W, R = Me or Ph) with I<sub>2</sub> affords the requisite iodometal carbenes  $[MI(CO)_2\{=C(OEt)R\}(\eta-C_5H_5)]$ .

Formation of the Carbenes  $[M(SnPh_3)(CO)_2 = C(OEt)Ph ](\eta - C_5H_5)]$  (M = Mo or W).—It was reported by others that the

 $<sup>\</sup>dagger$  Dicarbonyl[ethoxy(phenyl)methylene]( $\eta$ -pentamethylcyclopentadienyl)(triphenylstannyl)molybdenum and dicarbonyl( $\eta$ -cyclopentadienyl)[ethoxy(phenyl)methylene]iodotungsten.

Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1991, Issue 1, pp. xviii-xxii.



Scheme 1 (i) SnIR<sub>3</sub> (SnClPh<sub>3</sub> for 13 and 14), thf; (ii) (a) LiR', Et<sub>2</sub>O; (b)  $[OEt_3][BF_4]$ , water; (iii) I<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>



Fig. 1 The molecular structure of  $[Mo(SnPh_3)(CO)_2\{=C(OEt)Ph\}(\eta-C_5Me_5)]$  17

reaction of LiPh with  $[M(SnPh_3)(CO)_3(\eta-C_5H_5)]$  (M = Mo, 1; or W, 2) in 1,2-dimethoxyethane produces the acyls *trans*- $[M(SnPh_3)(COPh)(CO)_2(\eta-C_5H_5)]^{-,9}$  Unlike the iodo acyl  $[WI(COMe)(CO)_2(\eta-C_5H_5)]^{-}$ , these are thermally stable and isolable as their  $[NMe_4]^+$  salts (Scheme 1). Alkylation of these acyls with  $[OEt_3][BF_4]$  produces the expected carbenes 3 and 4, but in moderate yields (Scheme 1). It seems that the carbenes  $[M(SnPh_3)(CO)_2 = C(OEt)Me (\eta-C_5H_5)]$  (M = Mo or W) cannot be prepared by an analogous route using LiMe. Under the reported reaction conditions, addition of LiMe to the

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starting materials 1 and 2, followed by alkylation with  $[OEt_3][BF_4]$ , gives only 3 and 4 by an aryl for alkyl exchange process. We repeated these experiments under the reported conditions and found essentially similar results.

Using these conditions, complexes 3 and 4 are isolable in moderate yields (around 30%) and chromatography is required to remove [MEt(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (M = Mo or W) by-products and tin-containing impurities. We were able to enhance the yields of 3 and 4 by altering the reaction conditions. The yield of the carbene 3 is increased if Et<sub>2</sub>O is used as the reaction solvent. After alkylation with [OEt<sub>3</sub>][BF<sub>4</sub>] in water a high yield of 3 results (88%). Further, no by-products are formed. The improved method also works for LiMe. In this case, the carbenes [M(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] (M = Mo, 5; or W, 6) are isolated in good yields.

We note that the IR spectrum of the acyl [Mo(SnPh<sub>3</sub>)-(COPh)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> when formed in Et<sub>2</sub>O contains four carbonyl bands [v<sub>co</sub>(Et<sub>2</sub>O): 1905s, 1891(sh), 1825s and 1773 cm<sup>-1</sup>]. In tetrahydrofuran (thf) there are only two [v<sub>co</sub>(thf): 1892m and 1811s cm<sup>-1</sup>]. Further the relative IR band intensities in Et<sub>2</sub>O vary over a number of experiments, depending both on its concentration and the source of LiPh used to form it. This strongly implies that the acyl [Mo(SnPh<sub>3</sub>)(COPh)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> exists as a mixture of contact and solvent-separated ion pairs in Et<sub>2</sub>O.

This general methodology is tolerant to cyclopentadienyl functionality. Suitable precursors include complexes 7–10. The  $\eta$ -C<sub>5</sub>Me<sub>5</sub> and  $\eta^5$ -C<sub>9</sub>H<sub>7</sub> ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub> = indenyl) complexes [M(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] (M = Mo, 7; or W, 8) and [M(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)] (M = Mo, 9; or W, 10) are best made by the reaction of the anions [M(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)]<sup>-</sup> (M = Mo, 11; or W, 12) or [M(CO)<sub>3</sub>( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)]<sup>-</sup> (M = Mo, 13; or W, 14) with SnIPh<sub>3</sub>. Similarly, the reactions of the anions 11 and 12 with SnI(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub> lead to the complexes 15 and 16.

The reactions of  $[M(SnPh_3)(CO)_3(\eta-C_5Me_5)]$  (M = Mo, 7; or W, 8) with LiPh followed by  $[OEt_3][BF_4]$  result in the carbenes 17 and 18 while the corresponding reactions of the indenyl derivatives 9 and 10 lead to 19 and 20. Similarly, treatment of the complexes 15 and 16 with Li(C<sub>6</sub>H<sub>4</sub>Me-4) followed by alkylation with  $[OEt_3][BF_4]$  results in the carbenes 21 and 22.

The spectroscopic data for complexes 5, 6 and 17–22 are presented in Tables 1 and 2 together with data for 3 and 4 for comparison. The data are consistent with *trans* carbene complexes. No trace of corresponding *cis* isomers is detectable by IR or <sup>13</sup>C NMR spectroscopy. The steric demand of the SnPh<sub>3</sub> group presumably precludes the existence of *cis* isomers. This aspect is still under investigation. In every case, a high-frequency <sup>13</sup>C NMR carbene signal is seen. Where possible, phenyl signals in the <sup>13</sup>C NMR spectra of the complexes are assigned (Table 2) by comparison with known systems and by inspection of the *J*(SnC) couplings.

The X-ray structure of complex 17 is illustrated in Fig. 1. Atom coordinates, bond lengths and bond angles with estimated standard deviations are listed in Tables 3 and 4. The molecule comprises a molybdenum atom bonded in an essentially symmetric pentahapto manner to a  $\eta$ -C<sub>5</sub>Me<sub>5</sub> ligand (perpendicular distance of molybdenum from plane 2.045 Å; deviations of methyl carbon atoms by up to 0.35 Å in a direction away from the metal). The basal ligands comprise two mutually trans, linear carbonyls, a SnPh<sub>3</sub> ligand, and a carbene ligand {=C(OEt)Ph}, in which the phenyl group is located anti with respect to the  $\eta$ -C<sub>5</sub>Me<sub>5</sub> ligand, with the ethoxy group the most adjacent  $[O(3) \cdots C(17) 2.98 \text{ Å}]$ . The C(3)–O(3) bond is short (1.33 Å), as is the molybdenum-carbon bond to the carbene (2.11 A), suggesting some  $\pi$ -electron delocalisation. The plane of the carbene [O(3),C(3),C(6)] is inclined at 74° to the  $\eta$ -C<sub>5</sub>Me<sub>5</sub> ligand. There are no noteworthy contacts to the dichloromethane solvent molecules, or any other intermolecular contacts. The X-ray structure of the germyl complex [Mo- $(GePh_3)(CO)_2 = C(OEt)Ph (\eta - C_5H_5)$  is known.<sup>10</sup> In this

Table 1	Analytical	and of	her data	for the	complexes"

				Analysis (%)	
Complex	$IR/cm^{-1}$	M.p./°C	Mass spectrum <sup>b</sup>	С	Н
7	1989s, 1913(sh), 1899s	171–173	$[M - CO]^+, 638 (638)$	56.0 (55.9)	4.7 (4.5)
8	1985s, 1907(sh), 1893s	181–182	$[M - CO]^+, 724(724)$	49.6 (49.4)	4.1 (4.0)
9	2005s, 1937m, 1909m	143–145	$[M - CO]^+, 618 (618)$	55.7 (55.8)	3.6 (3.4)
10	1993s, 1925m, 1897s	149–152	$[M - CO]^+, 704 (704)$	49.4 (49.2)	3.1 (3.0)
15	1985s, 1911(sh), 1897s	195–197 (decomp.)	$[M - C_6 H_4 Me]^+, 617 (617)$	57.6 (57.7)	5.2 (5.1)
16	1981s, 1905(sh), 1889s	218-220	$[M - CO]^+, 766 (766)$	50.9 (51.3)	4.4 (4.5)
3	1949w, 1934m, 1886m, 1869s	148-150	$[M]^+, 702 (702)$	58.0 (58.2)	4.2 (4.3)
4	1946w, 1930m, 1882m, 1864s	162–164	[ <i>M</i> ] <sup>+</sup> , 788 (788)	52.0 (51.7)	4.1 (3.8)
5	1932m, 1867s	156–157	[ <i>M</i> ] <sup>+</sup> , 640 (640)	54.0 (54.5)	4.2 (4.4)
6	1929m, 1863s	168-171	[ <i>M</i> ] <sup>+</sup> , 726 (726)	47.4 (47.8)	3.6 (3.9)
17	1917m, 1853s	155–157 (decomp.)	$[M - H]^+, 771 (771)$	60.8 (60.7)°	5.2 (5.2)
18	1913m, 1845s	179–181	[M] <sup>+</sup> , 858 (858)	54.5 (54.5)	4.9 (4.7)
19	1943vw, 1929w, 1877m, 1863s	137–139	$[M - 2CO]^+, 696 (696)$	60.6 (60.7)	4.5 (4.3)
20	1937vw, 1925w, 1869m, 1857s	131–134	[ <i>M</i> ] <sup>+</sup> , 839 (839)	54.4 (54.4)	4.1 (3.8)
21	1915m, 1849s	182–184 (decomp.)	$[M]^+, 828 (828)$	62.5 (62.4)	5.8 (5.8)
22	1911m, 1845s	204–205	$[M - C_6 H_4 Me]^+, 823 (823)$	56.3 (56.4)	5.2 (5.2)
24	<i>cis</i> : 1970s, 1894s <i>trans</i> : 2007w, 1991w, 1941m, 1923s	72–74 (decomp.)	[ <i>M</i> ] <sup>+</sup> , 480 (480)	39.8 (40.2)	3.0 (3.2)
23	<i>cis</i> : 1963s, 1884s <i>trans</i> : 2002m, 1994m, 1989m, 1932s, 1923s, 1914s	118-120 (decomp.)	[ <i>M</i> ] <sup>+</sup> , 566 (566)	34.0 (34.0)	2.7 (2.7)
25	<i>cis</i> : 1969s, 1893s <i>trans</i> : 1991m, 1925s	88-90 (decomp.)	[ <i>M</i> ] <sup>+</sup> , 418 (418)	31.5 (31.7)	3.0 (3.1)
26	1987m, 1915s	100-102 (decomp.)	$[M]^+$ , 504 (504)	26.2 (26.2)	2.5 (2.6)
28	2009s, 1917s	133–135	[ <i>M</i> ] <sup>+</sup> , 394 (394)	58.6 (58.2)	5.3 (5.1)
29	2045s, 2009s	129–131	$[M - 2CO]^+, 614 (614)$	21.5 (21.6)	2.1 (2.2)

<sup>a</sup> Required values are in parentheses. <sup>b</sup> Highest observed ion pattern in mass spectrum, based on <sup>98</sup>Mo and <sup>184</sup>W isotopes. <sup>c</sup> Unsolvated sample.



structure, the carbene ligand adopts the same orientation as in that of complex 17.

The IR spectra of the complexes are interesting. Those of the carbene complexes 3, 4 and  $[Mo(GePh_3)(CO)_2 = C(OEt)Ph](\eta$ - $C_5H_5$ ] in cyclohexane each show four bands in the carbonyl region.<sup>10</sup> On the basis of <sup>13</sup>CO-labelling experiments involving the related complex trans-[Mo(GePh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Ph}(η- $C_5H_5$ ], these are assigned as isomers of type **a** and **b** (Scheme 2) generated by rotation about the M = C bond. The barrier to interconversion of these isomers (rotation about M=C) and the energy difference between them is very small. The IR spectra of the  $\eta$ -C<sub>5</sub>Me<sub>5</sub> complexes 17 and 18 show only two bands under similar conditions suggesting that, given the X-ray structure of 17, steric effects destabilize type b structures relative to type a structures for n-C5Me5 derivatives. The <sup>1</sup>H NMR spectra of 3 and 4 are known to be temperature independent in the range 20 to -80 °C. This phenomenon was not further examined in this work. However, satisfactory <sup>13</sup>C NMR spectra of 3 and 4 are obtained only at 20 °C. At -50 °C the signals due to the CO and CH<sub>2</sub> groups of 4 are not seen. This is a consequence of a fluxional process giving unobservably broad signals, presumably by the mechanism of Scheme 2.

The IR spectra of the carbenes 5 and 6 in cyclohexane also indicate the presence of just a single *trans* dicarbonyl. The spectrum of 5  $[v_{CO}(C_6H_{12}): 1932m \text{ and } 1867s \text{ cm}^{-1}]$  is similar to that of *trans*- $[Mo(GePh_3)(CO)_2{=C(OEt)Bu^t}(\eta-C_5H_5)]$  $[v_{CO}(C_6H_{12}): 1934m \text{ and } 1863s \text{ cm}^{-1}]$ , which almost certainly exists as only a type **a** isomer.<sup>9</sup> The inference is that complexes 5 and 6 exist in solution as type **a** isomers.

The carbenes *trans*- $[Co(GePh_3)(CO)_3[=C(OEt)R]]$  (R = alkyl or Ph)<sup>11</sup> and *cis*- $[Re(SnPh_3)(CO)_4[=C(OEt)R]]$  (R = aryl or NR'<sub>2</sub>)<sup>12</sup> are known. The rhenium carbenes are fluxional. In these cases the fluxional process is associated with interconversion between isomers differing in the orientation of the OEt group relative to the Re=C unit. This point is examined further below.

Metal-Tin Bond Cleavage by Iodine.—In general, metalmetal bonds undergo cleavage with halogens to form metal halide complexes.<sup>13</sup> For instance, the dirhenium carbene complexes  $[\text{Re}_2(\text{CO})_8 \{= \overline{\text{CO}(\text{CH}_2)_2}\text{O}\}_2]$  and  $[\text{Re}_2(\text{CO})_9 \{= \overline{\text{CO}(\text{CH}_2)_2}\text{O}\}]$  both react with Br<sub>2</sub> to give the carbene  $[\text{ReBr}(\text{CO})_4 \{= \overline{\text{CO}(\text{CH}_2)_2}\text{O}\}]$ .<sup>14</sup> The complexes  $[\text{M}(\text{SnMe}_3) \cdot (\text{CO})_3(\eta - \text{C}_5\text{H}_5)]$  (M = Cr, Mo or W) react with I<sub>2</sub> to generate  $[\text{MI}(\text{CO})_3(\eta - \text{C}_5\text{H}_5)]$  (M = Cr, Mo or W) and SnIMe<sub>3</sub>.<sup>15</sup> The reactions of  $[\text{M}(\text{SnPh}_3)(\text{CO}) \{= \text{C}(\text{OEt})\text{Ph}\}(\eta - \text{C}_5\text{H}_5)]$  (M = Fe or Ru) with I<sub>2</sub> lead to the iodides  $[\text{MI}(\text{CO}) \{= \text{C}(\text{OEt})\text{Ph}\} \cdot (\eta - \text{C}_5\text{H}_5)]$ .<sup>16</sup> By analogy, it was anticipated that the reaction of I<sub>2</sub> with the bimetallic carbenes 17–22 would give the corresponding iodometal carbenes, together with SnIPh<sub>3</sub>. This is the case for the  $\eta - \text{C}_5\text{H}_5$  complexes but the  $\eta - \text{C}_5\text{Me}_5$ complexes undergo complicated reactions giving a number of products (see below).

Addition of  $I_2$  to a  $CH_2Cl_2$  solution of the carbene 4 at -80 °C, followed by warming to room temperature, gives a deep red solution. Removal of  $CH_2Cl_2$ , followed by chromatography on silica, gives a quantitative yield of  $SnIPh_3$ .<sup>17</sup> The carbene 23

Table 2 Proton and <sup>13</sup>C NMR spectral data for the complexes

<sup>1</sup>H NMR<sup>a</sup> (δ) Complex

- 7.61-7.54 (m, 6 H, H<sup>2</sup> of Ph), 7.33-7.27 (m, 9 H, H<sup>3,4</sup> of Ph), 7 1.93 (s, 15 H,  $\eta$ -C<sub>5</sub>Me<sub>5</sub>) 7.59–7.54 (m, 6 H, H<sup>2</sup> of Ph), 7.34–7.27 (m, 9 H, H<sup>3.4</sup> of Ph),
- 8 2.05 (s, 15 H,  $\eta$ -C<sub>5</sub>Me<sub>5</sub>)
- 7.61 (m, 6 H,  $H^2$  of Ph), 7.38 (m, 9 H,  $H^{3,4}$  of Ph), 7.24 (m, 2 H, 9  $C_9H_7$ ), 7.04 (m, 2 H,  $C_9H_7$ ), 5.85 (d, 2 H, J 3,  $C_9H_7$ ), 5.12 (t, 1 H, J 3, C<sub>9</sub>H<sub>7</sub>)
- 7.65 (m, 6 H, H<sup>2</sup> of Ph), 7.35 (m, 9 H, H<sup>3.4</sup> of Ph), 7.25 (m, 2 H, 10 C<sub>9</sub>H<sub>7</sub>), 7.03 (m, 2 H, C<sub>9</sub>H<sub>7</sub>), 5.92 (d of d, 2 H, J 3, 1, C<sub>9</sub>H<sub>7</sub>), 5.21 (t, 1 H, J 3, C<sub>9</sub>H<sub>7</sub>) 7.46 [d, 6 H, J 8,  $J(^{119}SnH)$  44,  $J(^{117}SnH)$  42, H<sup>2</sup> of C<sub>6</sub>H<sub>4</sub>Me-
- 15 4], 7.13 (d, 6 H, J 8, H<sup>3</sup> of C<sub>6</sub>H<sub>4</sub>Me-4), 2.33 (s, 9 H, C<sub>6</sub>H<sub>4</sub>Me), 1.92 (s, 15 H,  $\eta$ -C<sub>5</sub>Me<sub>5</sub>) 7.46 [d, 6 H, J 8,  $J(^{119}SnH)$  44,  $J(^{117}SnH)$  42, H<sup>2</sup> of C<sub>6</sub>H<sub>4</sub>Me-
- 16 4], 7.12 (d, 6 H, J 8, H<sup>3</sup> of C<sub>6</sub>H<sub>4</sub>Me-4), 2.32 (s, 9 H, C<sub>6</sub>H<sub>4</sub>Me),
- 4],  $f_{12}$  (u, 0 H, 0 G, 1 d)  $f_{0,1}$  (u, 0 H, -C<sub>5</sub>Me<sub>5</sub>) 2.05 (s, 15 H, η-C<sub>5</sub>Me<sub>5</sub>) 7.64–7.57 (6 H, m, H<sup>2</sup> of SnPh), 7.42–7.26 (m, 12 H, H<sup>3,4</sup> of SnPh + =CPh), 6.98 (m, 2 H, H<sup>2</sup> of =CPh), 5.05 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 3 4.30 (q, 2 H, J 7, OCH<sub>2</sub>), 1.29 (t, 3 H, J 7, OCH<sub>2</sub>Me)
- 7.60–7.52 (m, 6 H, H<sup>2</sup> of SnPh), 7.32–7.25 (m, 12 H, H<sup>3.4</sup> of SnPh + =CPh), 6.99 (m, 2 H, H<sup>2</sup> of =CPh), 4.98 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.22 (q, 2 H, J 7, OCH<sub>2</sub>), 1.32 (t, 3 H, J 7, OCH<sub>2</sub>Me) 4
- 7.63-7.57 (m, 6 H, H<sup>2</sup> of Ph), 7.36-7.27 (m, 9 H, H<sup>3,4</sup> of Ph), 5.31 5  $(s, 5 H, C_5H_5, 4.33 (q, 2 H, J7, OCH_2), 2.91 (s, 3 H, = CMe), 1.42 (t, 3 H, J7, OCH_2Me)$
- 7.62–7.55 (m, 6  $\tilde{H}$ , H<sup>2</sup> of Ph), 7.37–7.26 (m, 9 H, H<sup>3,4</sup> of Ph), 6 5.38 (s, 5 H,  $C_5H_5$ ), 4.28 (q, 2 H, J 7, OCH<sub>2</sub>), 2.83 (s, 3 H, =CMe), 1.46 (t, 3 H, J 7, OCH<sub>2</sub>Me)
  - 7.54-7.47 (m, br, 6 H, H<sup>2</sup> of SnPh), 7.33-7.14 (m, 12 H, H<sup>3,4</sup> of SnPh + = CPh), 6.82 (m, 2 H, H<sup>2</sup> of = CPh), 4.11 (q, 2 H, J 7,  $OCH_2$ ), 1.91 (s, 15 H,  $\eta$ -C<sub>5</sub>Me<sub>5</sub>), 1.52 (t, 3 H, J 7,  $OCH_2Me$ )
- 7.50-7.42 (m, br, 6 H, H<sup>2</sup> of SnPh), 7.38-7.12 (m, 12 H, H<sup>3,4</sup> of 18 SnPh + = CPh), 6.88 (m, 2 H, H<sup>2</sup> of = CPh), 4.10 (q, 2 H, J 7,  $OCH_2$ ), 2.03 (s, 15 H,  $\eta$ -C<sub>5</sub>Me<sub>5</sub>), 1.49 (t, 3 H, J 7,  $OCH_2Me$ )
- 7.65 (m, 6 H, H<sup>2</sup> of Ph), 7.5-7.35 (m, 3 H, H<sup>3,4</sup> of =CPh), 7.34 (m, 19 9 H,  $H^{3,4}$  of Ph), 6.98 (m, 2 H,  $H^2$  of =CPh), 6.78 (m, 2 H,  $C_9H_7$ ), 6.59 (m, 2 H, C<sub>9</sub>H<sub>7</sub>), 5.64 (d of d, 2 H, J 3, 1, C<sub>9</sub>H<sub>7</sub>), 5.39 (t, 1 H, J 3,  $C_9H_7$ ), 4.05 (q, 2 H, J 7, OCH<sub>2</sub>), 1.33 (t, 3 H, J 7, OCH<sub>2</sub>Me) 7.58 (m, 6 H, H<sup>2</sup> of Ph), 7.45–7.32 (m, 3 H, H<sup>3,4</sup> of =CPh), 7.30 (m, 20
  - 9 H, H<sup>3,4</sup> of Ph), 6.95 (m, 2 H, H<sup>2</sup> of =CPh), 6.85–6.75 (m, 4 H, C<sub>9</sub>H<sub>7</sub>), 5.82 (d, 2 H, J 3, C<sub>9</sub>H<sub>7</sub>), 5.61 (t, 1 H, J 3, C<sub>9</sub>H<sub>7</sub>), 4.01 (q, 2 H, J7, OCH<sub>2</sub>), 1.41 (t, 3 H, J7, OCH<sub>2</sub>Me)
- $\begin{array}{l} \text{H, } J^{*}, \text{ } \text{OCH}_{2}, \text{H, } H^{*}(\textbf{i}, \textbf{S} \textbf{h}, \textbf{J}^{*}, \text{OCH}_{2}Me^{\prime}) \\ \text{7.38} (d, 2 \text{ H, } J^{*}, \text{H}^{2} \text{ of } \text{SnC}_{6}\text{H}_{4}\text{Me}^{*} \textbf{h}, \text{7.09} (d, 2 \text{ H, } J^{*} \textbf{s}, \text{H}^{3} \text{ of } \text{sc}_{6}\text{C}_{6}\text{H}_{4}\text{Me}^{*} \textbf{h}, \text{7.00} (d, 2 \text{ H, } J^{*}, \text{H}^{3} \text{ of } \text{SnC}_{6}\text{H}_{4}\text{Me}^{*} \textbf{h}), \text{6.73} (d, 2 \text{ H, } J^{*} \textbf{s}, \text{H}^{2} \text{ of } \text{sc}_{6}\text{C}_{6}\text{H}_{4}\text{Me}^{*} \textbf{h}, \text{4.10} (\textbf{q}, 2 \text{ H, } J^{*}, \text{OCH}_{2}), \text{2.37} (\textbf{s}, 3 \text{ H, } \text{sc}_{6}\text{H}_{4}Me), \text{1.90} (\textbf{s}, \text{15} \text{ H, } \text{\eta}\text{-}\text{C}_{5}\text{Me}_{5}), \text{1.50} (\textbf{t}, 3 \text{ H, } J^{*}, \text{OCH}_{2}Me) \end{array}$ 21
- 22 7.34 (d, br, 2 H, J 7, H<sup>2</sup> of  $SnC_{6}H_{4}Me-4$ ), 7.16 (d, 2 H, J 8, H<sup>3</sup> of  $=CC_6H_4Me-4$ ), 6.98 (d, br, 2 H, J 7, H<sup>3</sup> of SnC<sub>6</sub>H<sub>4</sub>Me-4), 6.80 (d, 2 H, J 8, H<sup>2</sup> of  $=CC_6H_4Me.4$ ), 4.02 (q, 2 H, J 7, OCH<sub>2</sub>), 2.43 (s, 3 H,  $=CC_6H_4Me$ ), 2.28 (s, 9 H,  $SnC_6H_4Me$ ), 2.03 (s, 15 H, η-C<sub>5</sub>Me<sub>5</sub>), 1.48 (t, 3 H, J7, OCH<sub>2</sub>Me)
- cis: 7.44-7.25 (m, 3 H, H<sup>3,4</sup> of Ph), 7.17 (m, 2 H, H<sup>2</sup> of Ph), 5.34 24 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.97 (d of q, 1 H, J 11, 7, OCH<sub>2</sub>), 4.65 (d of q, 1 H, J 11, 7, OCH<sub>2</sub>), 1.58 (t, 3 H, OCH<sub>2</sub>Me) trans: 7.44–7.25 (m, 3 H, H<sup>3,4</sup> of Ph), 6.90 (m, 2 H, H<sup>2</sup> of Ph), 5.36 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.07 (q, 2 H, J 7, OCH<sub>2</sub>), 1.39 (t, 3 H, J 7, OCH<sub>2</sub>Me)

<sup>13</sup>C NMR<sup>b</sup> (δ)

- <sup>c</sup> 232.9 (1 CO), 227.6 (2 CO), 136.9 (br, Ph-*o*), 127.9 (br, Ph-*p* + -m), 103.8 ( $C_5$ Me<sub>5</sub>), 11.2 ( $C_5$ Me<sub>5</sub>)
- <sup>c</sup> 221.6 (1 CO), 218.3 (2 CO), 137.0 (br, Ph-o), 127.9 (br, Ph-p + -m), 102.3 ( $C_5 Me_5$ ), 11.2 ( $C_5 Me_5$ )
- 227.8 (1 CO), 223.6 (2 CO), 141.9 (Ph-i), 136.5 (Ph-o), 128.6 (Ph-p), 128.3 (Ph-m), 125.6 (C<sub>9</sub>H<sub>7</sub>), 123.6 (C<sub>9</sub>H<sub>7</sub>), 108.8  $(C_9H_7)$ , 93.1  $(C_9H_7)$ , 79.7  $(C_9H_7)$
- 216.5 (1 CO), 213.2 (2 CO), 141.3 (Ph-i), 136.6 (Ph-o), 128.6 (Ph-p), 128.2 (Ph-m), 126.4 (C<sub>9</sub>H<sub>7</sub>), 123.7 (C<sub>9</sub>H<sub>7</sub>), 107.4  $(C_9H_7)$ , 91.0  $(C_9H_7)$ , 78.0  $(C_9H_7)$
- <sup>6</sup> 233.1 (1 CO), 227.7 (2 CO), 137.8 (C<sup>4</sup> of C<sub>6</sub>H<sub>4</sub>Me-4), 128.8 [J(SnC) 44, C<sup>2.3</sup> of C<sub>6</sub>H<sub>4</sub>Me-4], 103.7 (C<sub>5</sub>Me<sub>5</sub>), 21.5 (C<sub>6</sub>H<sub>4</sub>-Me), 11.2 (C<sub>5</sub>Me<sub>5</sub>)
- <sup>c</sup> 221.9 (1 CO), 218.4 (2 CO), 137.8 (C<sup>4</sup> of C<sub>6</sub>H<sub>4</sub>Me-4), 128.8 [J(SnC) 45, C<sup>2,3</sup> of C<sub>6</sub>Me-4], 102.3 (C<sub>5</sub>Me<sub>5</sub>), 21.5 (C<sub>6</sub>H<sub>4</sub>Me),  $11.2 (C_5 Me_5)$
- <sup>4</sup> 328.8 (Mo=C), 227.3 (CO), 154.5 (=CPh-*i*), 144.0 [s, J(SnC)357, SnPh-*i*), 136.9 [s, J(SnC) 35, C<sup>2</sup> of SnPh], 129.9 [s, J(SnC)60, C<sup>3.4</sup> of SnPh + C<sup>4</sup> of = CPh], 127.6 (C<sup>3</sup> of =CPh), 121.6 (C<sup>2</sup> of =CPh), 94.1 (C<sub>5</sub>H<sub>5</sub>), 73.6 (OCH<sub>2</sub>), 15.2 (OCH<sub>2</sub>Me)
- <sup>d</sup> 306.1 (W=C), 218.6 (CO), 154.9 (=CPh-i), 143.6 [J(SnC)356, SnPh-*i*], 137.0 [*J*(SnC) 27, C<sup>2</sup> of SnPh], 127.9 [*J*(SnC) 58, C<sup>3,4</sup> of SnPh + C<sup>4</sup> of =CPh], 127.5 (C<sup>3</sup> of =CPh), 121.6 (C<sup>2</sup> of =CPh), 93.1 (C<sub>5</sub>H<sub>5</sub>), 73.1 (OCH<sub>2</sub>), 15.2 (OCH<sub>2</sub>Me)
- <sup>*a*</sup> 332.9 (Mo=C), 229.2 (CO), 144.5 [*J*(SnC) 348, Ph-*i*], 136.9 [*J*(SnC) 35, C<sup>2</sup> of Ph], 127.9 [*J*(SnC) 43, C<sup>3</sup> of Ph], 127.8 (C<sup>4</sup> of Ph), 93.7 (C<sub>5</sub>H<sub>5</sub>), 71.3 (OCH<sub>2</sub>), 45.1 (=CMe), 14.8 (OCH<sub>2</sub>Me) 307.4 (W=C), 221.6 (CO), 143.8 [J(SnC) 365, Ph-i], 136.7 [J(SnC) 34, C<sup>2</sup> of Ph], 127.8 [J(SnC) 41, C<sup>3.4</sup> of Ph], 93.2 (C<sub>5</sub>H<sub>5</sub>), 69.2 (OCH<sub>2</sub>), 46.4 (=CMe), 14.5 (OCH<sub>2</sub>Me)
- ( $c_5 n_5$ ), 05.2 (OC  $n_2$ ), 40.4 (= CMe), 14.5 (OC  $n_2 Me$ ) <sup>e</sup> 327.8 (Mo=C), 232.4 (2 CO), 150.1 (=CPh-i), 146.2 (SnPh-i), 143.9 (SnPh-i), 137.6 (C<sup>2</sup> of SnPh), 137.1 (C<sup>2</sup> of SnPh), 136.3 (C<sup>4</sup> of =CPh), 127.8 (C<sup>4</sup> of SnPh), 127.6 (C<sup>4</sup> of SnPh), 127.5, (C<sup>3</sup> of SnPh), 127.2 (C<sup>3</sup> of SnPh), 126.8 (C<sup>3</sup> of =CPh), 119.6 (C<sup>2</sup> of =CPh), 105.1 ( $C_5 Me_5$ ), 73.3 (OCH<sub>2</sub>), 15.2 (OCH<sub>2</sub>Me), 11.4 ( $C_5Me_5$ )
- e 304.2 (W=C), 225.6 [J(WC) 160, 2 CO], 152.0 (=CPh-i), 146.0 (SnPh-i), 142.3 (SnPh-i), 137.6  $(\text{C}^2 \text{ of SnPh})$ , 137.4  $(\text{C}^2 \text{ of SnPh})$ , 136.4  $(\text{C}^4 \text{ of =CPh})$ , 127.6  $(\text{C}^4 \text{ of SnPh})$ , 137.4  $(\text{C}^2 \text{ of SnPh})$ , 136.4  $(\text{C}^4 \text{ of =CPh})$ , 127.6  $(\text{C}^4 \text{ of SnPh})$ , 127.5  $(\text{C}^4 \text{ of SnPh})$ , 127.2  $(\text{C}^3 \text{ of SnPh})$ , 127.0  $(\text{C}^3 \text{ of SnPh})$ , 126.8  $(\text{C}^3 \text{ of SnPh})$ , 126.8  $(\text{C}^3 \text{ of SnPh})$ , 127.9  $(\text{C}^3 \text{ of SnPh})$ , 128.9  $(\text{C}^3 \text{ of SnPh})$ , =CPh), 119.6 (C<sup>2</sup> of =CPh), 104.4 (C<sub>5</sub>Me<sub>5</sub>), 72.5 (OCH<sub>2</sub>), 15.1 (OCH<sub>2</sub>Me), 11.5 (C<sub>5</sub>Me<sub>5</sub>)
- <sup>f</sup>137-125 (Ph), 110.6 (C<sub>9</sub>H<sub>7</sub>), 95.3 (C<sub>9</sub>H<sub>7</sub>), 85.3 (C<sub>9</sub>H<sub>7</sub>), 15.0 (Me)

<sup>f</sup> 221.7 (CO), 143.3 (SnPh-i), 137.0 (=CPh-i), 137-120 (Ph), 109.2  $(C_9H_7)$ , 94.2  $(C_9H_7)$ , 84.2  $(C_9H_7)$ , 73.0  $(OCH_2)$ , 15.1 (Me)

329.7 (Mo=C), 232.5 (2 CO), 148.6 (C<sup>i</sup> of = $CC_6H_4Me-4$ ), 141.6 (C<sup>i</sup> of  $SnC_6H_4Me-4$ ), 137.5 [J(SnC) 35.5, C<sup>2</sup> of  $SnC_6H_4Me-4$ ), 137.5 [J(SnC) 35.5, C<sup>2</sup> of  $SnC_6H_4Me-4$ ) 4], 136.7 (C<sup>4</sup> of =CC<sub>6</sub>H<sub>4</sub>Me-4), 136.6 (C<sup>4</sup> of SnC<sub>6</sub>H<sub>4</sub>Me-4), 128.3 [J(SnC) 42.5, C<sup>3</sup> of SnC<sub>6</sub>H<sub>4</sub>Me-4 + =CC<sub>6</sub>H<sub>4</sub>Me-4], 120.4 (C<sup>2</sup> of =CC<sub>6</sub>H<sub>4</sub>Me-4), 105.3 ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>), 72.8 (OCH<sub>2</sub>), 21.4 (SnC<sub>6</sub>H<sub>4</sub>Me), 21.2 (=CC<sub>6</sub>H<sub>4</sub>Me), 15.4 (OCH<sub>2</sub>Me), 11.4 (η- $C_5Me_5$ 

304.8 (W=C), 225.8 (2 CO), 149.8 (C<sup>i</sup> of =CC<sub>6</sub>H<sub>4</sub>Me-4), 139.5 (C<sup>i</sup> of SnC<sub>6</sub>H<sub>4</sub>Me-4), 137.5 [J(SnC) 35.0, C<sup>2</sup> of SnC<sub>6</sub>H<sub>4</sub>Me-4], 137.1 (C<sup>4</sup> of =CC<sub>6</sub>H<sub>4</sub>Me-4), 136.3 (C<sup>4</sup> of SnC<sub>6</sub>H<sub>4</sub>Me-4), 128.4 [J(SnC) 42.5, C<sup>3</sup> of SnC<sub>6</sub>H<sub>4</sub>Me-4], 127.9 (C<sup>3</sup> of =CC<sub>6</sub>H<sub>4</sub>-Me-4), 119.6 (C<sup>2</sup> of =CC<sub>6</sub>H<sub>4</sub>Me-4), 104.3 ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>), 72.1 (OCH<sub>2</sub>), 21.5 (SnC<sub>6</sub>H<sub>4</sub>Me), 21.2 (=CC<sub>6</sub>H<sub>4</sub>Me), 15.0 (OCH<sub>2</sub>-*Me*), 11.4 ( $\eta$ -C<sub>5</sub>*Me*<sub>5</sub>)

<sup>*a*</sup> 323.8 (Mo=C), 224.1 (CO), 151.6 (C<sup>i</sup> of Ph), 129.9 (C<sup>4</sup> of Ph), 129.0 (C<sup>3</sup> of Ph), 121.9 (C<sup>2</sup> of Ph), 98.5 (C<sub>5</sub>H<sub>5</sub>), 74.7 (OCH<sub>2</sub>), 14.6 (OCH<sub>2</sub>Me)

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## Table 2 (continued)

Complex	<sup>1</sup> H NMR <sup><i>a</i></sup> (δ)	<sup>13</sup> C NMR <sup><math>b</math></sup> ( $\delta$ )
23	<i>cis</i> : 7.46–7.23 (m, 3 H, H <sup>3,4</sup> of Ph), 7.13 (m, 2 H, H <sup>2</sup> of Ph), 5.51 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 5.01 (d of q, 1 H, <i>J</i> 7, OCH <sub>2</sub> ), 4.63 (d of q, 1 H, <i>J</i> 11, 7, OCH <sub>2</sub> ), 1.59 (t, 3 H, <i>J</i> 7, OCH <sub>2</sub> <i>Me</i> ) <i>trans</i> : 7.46–7.23 (m, 3 H, H <sup>3,4</sup> of Ph), 6.94 (m, 2 H, H <sup>2</sup> of Ph), 5.54 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 3.86 (q, 2 H, <i>J</i> 7, OCH <sub>2</sub> ), 1.35 (t, 3 H, <i>J</i> 7, OCH <sub>4</sub> <i>Me</i> )	<sup><i>θ</i></sup> trans: 299.7 (W=C), 216.6 (CO), 152.3 (C <sup>i</sup> of Ph), 128.9 (C <sup>4</sup> of Ph), 128.8 (C <sup>3</sup> of Ph), 122.5 (C <sup>2</sup> of Ph), 97.5 (η-C <sub>5</sub> H <sub>5</sub> ), 73.1 (OCH <sub>2</sub> ), 15.4 (OCH <sub>2</sub> Me) cis: 98.8 (η-C <sub>5</sub> H <sub>5</sub> ) (only visible signal)
25	<i>cis</i> : 5.69 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 4.74 (d of q, 1 H, J 10, 7, OCH <sub>2</sub> ), 4.50 (d of q, 1 H, J 10, 7, OCH <sub>2</sub> ), 3.20 (s, 3 H, =CMe), 1.55 (t, 3 H, J 7, OCH <sub>2</sub> Me) <i>trans</i> : 5.51 (s, 5 H, C <sub>5</sub> H <sub>5</sub> ), 4.26 (q, 2 H, J 7, OCH <sub>2</sub> ), 2.97 (s, 3 H, =CMe), 1.53 (t, 3 H, J 7, OCH <sub>2</sub> Me)	324.7 (Mo=C), 225.0 (CO), 97.8 (C <sub>5</sub> H <sub>5</sub> ), 70.4 (OCH <sub>2</sub> ), 45.1 (=C <i>Me</i> ), 14.2 (OCH <sub>2</sub> <i>Me</i> )
26	5.61 (s, 5 H, $C_5H_5$ ), 4.17 (q, 2 H, $J$ 7, OCH <sub>2</sub> ), 2.95 (s, 3 H, =CMe), 1.47 (t, 3 H, $J$ 7, OCH <sub>2</sub> $Me$ )	<sup>h</sup> 296.4 (W=C), 217.2 [s, J(WC) 172, CO], 94.5 (C <sub>5</sub> H <sub>5</sub> ), 67.4 (OCH <sub>2</sub> ), 43.4 (=CMe), 11.0 (OCH <sub>2</sub> Me)
28	7.68–7.62 (m, 2 H, H <sup>2</sup> of Ph), 7.16–7.00 (m, 3 H, H <sup>3.4</sup> of Ph), 1.78 (s, 15 H, $\eta$ -C <sub>5</sub> Me <sub>5</sub> )	242.2 (2 CO), 230.0 (1 CO), 150.7 (C <sup>i</sup> of Ph), 144.6 (C <sup>2</sup> of Ph), 128.3 (C <sup>4</sup> of Ph), 124.3 (C <sup>3</sup> of Ph), 105.5 ( $\eta$ -C <sub>5</sub> Me <sub>5</sub> ), 10.6 ( $\eta$ -C <sub>5</sub> Me <sub>5</sub> )
29	2.28 (s, 15 H, $\eta$ -C <sub>5</sub> Me <sub>5</sub> )	5 57

" In CDCl<sub>3</sub> at ambient temperature unless stated otherwise; J in Hz. " In CDCl<sub>3</sub> at 223 K unless otherwise stated. " ipso-Carbon not visible in spectrum.<sup>d</sup> At ambient temperature.<sup>e</sup> Signals doubled up owing to hindered rotation of the SnPh<sub>3</sub> group about the M-Sn bond. <sup>f</sup> Fluxional system at this temperature, hence missing signals. <sup>*g*</sup> In  $[{}^{2}H_{6}]$  acetone at ambient temperature. <sup>*h*</sup> In  $[{}^{2}H_{6}]$  acetone at -80 °C.

Table 3 Atom coordinates  $(\times 10^4)$  for  $[Mo(SnPh_3)(CO)_2 = C(OEt)Ph (\eta - C_5Me_5)]$  17

Atom	x	У	Ζ	Atom	x	у	z
Sn	2591(2)	2870(1)	399(1)	C(21)	4666(22)	562(20)	819(19)
Mo	2368(2)	1216(2)	631(1)	C(22)	1696(14)	3607(13)	1068(13)
<b>O</b> (1)	3347(18)	1952(15)	2284(12)	C(23)	1414(14)	4342(13)	727(13)
O(2)	404(13)	1916(15)	267(13)	C(24)	794(14)	4810(13)	1111(13)
O(3)	1411(17)	-126(13)	1376(12)	C(25)	456(14)	4544(13)	1837(13)
C(1)	2989(22)	1682(18)	1667(18)	C(26)	738(14)	3810(13)	2178(13)
C(2)	1157(20)	1700(15)	402(14)	C(27)	1358(14)	3342(13)	1794(13)
C(3)	1614(21)	641(16)	1496(16)	C(28)	2258(15)	3333(11)	-873(9)
C(4)	965(26)	-622(21)	2003(20)	C(29)	1359(15)	3250(11)	-1248(9)
C(5)	764(29)	-1403(24)	1672(25)	C(30)	1121(15)	3541(11)	-2050(9)
C(6)	1346(15)	990(12)	2286(10)	C(31)	1784(15)	3914(11)	-2476(9)
C(7)	1898(15)	930(12)	3041(10)	C(32)	2683(15)	3996(11)	-2101(9)
C(8)	1602(15)	1255(12)	3760(10)	C(33)	2921(15)	3706(11)	-1300(9)
C(9)	753(15)	1642(12)	3724(10)	C(34)	3990(12)	3356(13)	783(11)
C(10)	201(15)	1702(12)	2968(10)	C(35)	4096(12)	4178(13)	722(11)
C(11)	498(15)	1377(12)	2250(10)	C(36)	4954(12)	4526(13)	948(11)
C(12)	3038(15)	- 36(10)	310(11)	C(37)	5704(12)	4051(13)	1234(11)
C(13)	2315(15)	149(10)	-318(11)	C(38)	5598(12)	3228(13)	1295(11)
C(14)	2568(15)	848(10)	- 733(11)	C(39)	4740(12)	2880(13)	1070(11)
C(15)	3447(15)	1094(10)	- 362(11)	Cl(1)	3200(16)	862(10)	5986(17)
C(16)	3737(15)	548(10)	283(11)	Cl(2)	3212(16)	2530(10)	6230(17)
C(17)	3135(23)	-784(18)	810(18)	C(40)	3684(16)	1753(10)	5716(17)
C(18)	1470(22)	- 351(20)	- 558(19)	Cl(3)	3401(44)	2103(43)	4858(26)
C(19)	2058(25)	1156(22)	-1556(20)	Cl(4)	3277(44)	2165(43)	6589(26)
C(20)	4046(21)	1661(17)	-750(17)	C(41)	3813(44)	1708(43)	5813(26)

Atoms [Cl(1), Cl(2), C(40)] and [Cl(3), Cl(4), C(41)], and their associated hydrogens comprise two fractional-occupancy (0.66, 0.34) dichloromethane molecules of solvation which occupy mutually incompatible sites.

remains adsorbed on the SiO<sub>2</sub>. Fortunately, charomatography at -80 °C on Al<sub>2</sub>O<sub>3</sub> affords the pure carbene 23, while in this case it is the SnIPh<sub>3</sub> that is strongly retained.

The IR spectrum of the tungsten compound 23 in  $C_6H_{12}$  is illustrated in Fig. 2. Four dicarbonyls coexist, three trans and one cis. The cis: trans ratio is solvent dependent. Infrared spectra recorded immediately after dissolution of 23 are identical to those recorded later. Equilibrium between the cis and *trans* isomers is therefore achieved very rapidly at room temperature. Only one geometry is seen in the solid-state structure as shown by an X-ray diffraction study (Fig. 3). The molecule comprises a tungsten atom to which is co-ordinated an iodine, a symmetric  $\eta$ -C<sub>5</sub>H<sub>5</sub> (perpendicular distance of tungsten from ring plane is 1.971 Å) and two essentially linear carbonyl ligands. The carbene ligand is positioned so that the phenyl group is anti with respect to the cyclopentadienyl ligand. A similar geometry is found for the phenyl group in a number of other carbene complexes.<sup>10,18</sup> The W–C–X (X = C or O) bond

angles at the carbone carbon atom are equal. The phenyl fragment is twisted by  $97^{\circ}$  from the plane defined by atoms O(3), C(8), C(9). The trans-basal bond angle between iodine and carbene is large at 143°

Given the evidence of four isomers in the IR spectrum, it is not too surprising that complex 23 is fluxional. There are two factors to consider, the interconversion of cis and trans isomers (the terminology cis and trans referring to the mutual carbonyl orientation), and the carbene orientation. At ambient temperature the <sup>1</sup>H NMR spectrum of 23 in CDCl<sub>3</sub> shows sets of signals for one cis and one trans complex in the ratio 12:88.

Complexes of the type  $[M(CO)_2A(B)(\eta-C_5H_5)]$  are known to undergo cis-trans isomerization on NMR time-scales, often above ambient temperature.<sup>19</sup> This process for 23 must take place at a temperature higher than 60 °C (the experimental temperature limit in CDCl<sub>3</sub> and at which thermal decomposition is evident).

The signals of the trans component show temperature

deviations (e.s.d.s) for $[Mo(SnPh_3)(CO)_2 = C(OEt)Ph (\eta - C_5Me_5)]$ 17					
Sn-Mo	2.827(6)	Sn-C(22)	2.170(23)		
Sn-C(28)	2.205(16)	SnC(34)	2.227(18)		
$Mo-\dot{C}(1)$	1.982(29)	MoC(2)	1.946(28)		
Mo-C(3)	2.105(29)	Mo-C(12)	2.399(19)		
Mo-C(13)	2.355(18)	Mo-C(14)	2.341(19)		
Mo-C(15)	2.376(22)	Mo-C(16)	2.411(22)		
O(1)-C(1)	1.168(35)	O(2)-C(2)	1.157(34)		
O(3)-C(3)	1.331(35)	O(3)-C(4)	1.513(42)		
C(3)-C(6)	1.495(33)	C(4)-C(5)	1.434(53)		
C(12)-C(17)	1.492(34)	C(13)-C(18)	1.509(38)		
C(14)-C(19)	1.545(37)	C(15)-C(20)	1.478(36)		
C(16)-C(21)	1.531(36)	C-C(phenyl)	1.395		
$C-C(\eta-C_5Me_5)$	1.420	C-Cl	1.730		
$M_0 = S_{n} = C(22)$	114 2(6)	$M_0 - S_n - C(28)$	116 9(5)		
C(22) = Sn = C(28)	100 4(8)	$M_0 = S_n = C(34)$	116.0(6)		
C(22)-Sn-C(34)	103.6(8)	C(28)-Sn-C(34)	103.7(7)		
Sn-Mo-C(1)	71.0(9)	Sn-Mo-C(2)	71.3(8)		
$C(1)-M_0-C(2)$	108.8(12)	Sn-Mo-C(3)	127.9(8)		
C(1) - Mo - C(3)	81.0(12)	C(2)-Mo-C(3)	77.8(11)		
C(3)-O(3)-C(4)	122.6(23)	Mo-C(1)-O(1)	179.1(24)		
Mo-C(2)-O(2)	173.6(23)	Mo-C(3)-O(3)	118.0(19)		
Mo-C(3)-C(6)	126.3(18)	O(3)-C(3)-C(6)	115.5(23)		
O(3) - C(4) - C(5)	109.8(29)	C(3)-C(6)-C(7)	122.7(13)		
C(3)-C(6)-C(11)	117.3(13)	C(13)-C(12)-C(17)	126.4(14)		
C(16)-C(12)-C(17)	124.8(15)	C(12)-C(13)-C(18)	126.0(13)		
C(14)-C(13)-C(18)	125.7(13)	C(13)-C(14)-C(19)	124.0(16)		
C(15)-C(14)-C(19)	126.8(16)	C(14)-C(15)-C(20)	123.9(13)		
C(16)-C(15)-C(20)	125.7(13)	C(12)-C(16)-C(21)	126.2(14)		
C(15)-C(16)-C(21)	125.8(14)	Sn-C(22)-C(23)	118.4(6)		
Sn-C(22)-C(27)	121.5(6)	Sn-C(28)-C(29)	118.4(6)		
Sn-C(28)-C(33)	121.6(6)	Sn-C(34)-C(35)	116.7(6)		
Sn-C(34)-C(39)	123.3(6)	C-C-C(phenyl)	120.0		
$C-C-C(\eta-C_5Me_5)$	108.0	Cl-C-Cl	109.6		





Fig. 2 The solution IR spectrum (cyclohexane) of  $[WI(CO)_2-{=C(OEt)Ph}(\eta-C_5H_5)]$  23 in the carbonyl region

dependence in the range -80 to 60 °C. The ambienttemperature spectrum is not quite at the high-temperature limit for the *trans* component. At 60 °C, the spectrum of this component is sharp. On cooling below room temperature, the signals broaden and split into two at about -80 °C in  $[^{2}H_{6}]$  acetone. The two *trans* C<sub>5</sub>H<sub>5</sub> signals are in the ratio 67:33 at -80 °C in  $[^{2}H_{6}]$  acetone but in CDCl<sub>3</sub> at -45 °C, they are exchange broadened by about 12 Hz and in the ratio 48:52. While there is clear IR evidence of a third *trans* component, no <sup>1</sup>H NMR evidence is available at -80 °C. Further cooling is impractical as the  $[^{2}H_{6}]$  acetone freezes. Thus, the lowtemperature-limiting spectrum cannot be recorded.

The presence of three *trans* isomers in the IR spectrum requires an additional source of isomerism to the two generated by M=C rotation. A plausible source is suggested by the fact that some carbene complexes (see above) are fluxional as a consequence of differences in OEt orientation. A combination of



Fig. 3 Molecular structure of  $[WI(CO)_2 = C(OEt)Ph](\eta - C_5H_5)]$  23

these two sources of isomerism suggests the four structural possibilities of Scheme 2. One of these,  $\mathbf{d}$ , is excluded on the grounds that the ethyl group will interfere unfavourably with the  $\eta$ -C<sub>5</sub>H<sub>5</sub> group, leaving three, **a**-**c**, as observed in the IR spectrum.

Using the variable-temperature <sup>1</sup>H NMR data in CDCl<sub>3</sub>, an activation energy,  $\Delta G^{\ddagger}$ , can be calculated using simple equations.<sup>20,21</sup> These give a value of  $\Delta G^{\ddagger} = 48 \pm 3$  kJ mol<sup>-1</sup>. It is not clear whether this value is associated with M=C rotation or differences in OEt orientation since the energies for the two processes are rather similar on inspection of the available data (for instance: M=C rotation, *cis*-[Cr(CO)<sub>4</sub>{=CN(Me)CH<sub>2</sub>CH<sub>2</sub>NMe}<sub>2</sub>] 48.5; *cis*- [W(CO)<sub>4</sub>-{=CN(Me)CH<sub>2</sub>CH<sub>2</sub>NMe)<sub>2</sub>], 43.5; [Fe(=CH<sub>2</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>PPh<sub>2</sub>)(η-C<sub>5</sub>H<sub>5</sub>)]<sup>+</sup>, 43.5;<sup>21</sup> OEt orientation, [Cr(CO)<sub>5</sub>-{=C(OMe)Ph}], 52.9; [Cr(CO)<sub>5</sub>{=C(OMe)(C<sub>6</sub>H<sub>4</sub>Me-4)}], 49.1;<sup>22</sup> [Cr(CO)<sub>5</sub>{=C(OMe)Me}],<sup>23</sup> 56.7 kJ mol<sup>-1</sup>). Whichever process this value for compound 23 is associated with, the activation energy of the second process is probably low as it is not frozen out at -80 °C. The similarity of these activation energies suggests a re-examination of the origin of the fluxionality of complexes 3 and 4 might be useful.

In the <sup>13</sup>C NMR spectrum of complex **23** at -80 °C in [<sup>2</sup>H<sub>6</sub>]acetone two major C<sub>5</sub>H<sub>5</sub> signals are seen. These are assigned to *trans* components. Two sets of Me, CH<sub>2</sub>, *ipsophenyl*, and carbene signals are associated with the C<sub>5</sub>H<sub>5</sub> peaks. These signals are in the same ratio as those in the <sup>1</sup>H NMR spectrum. Only traces of the *cis* isomer of **23** are detected ( $\delta_c$  98.8, C<sub>5</sub>H<sub>5</sub>). Signal overlaps prevent complete assignment of the spectrum (see Table 2).

Essentially identical results are obtained for the reaction of  $I_2$  with the molybdenum carbene 3 in which case the product is 24. The product is maroon and exists as a mix of *cis* and *trans* isomers. The IR spectra of the carbene complexes 23 and 24 in cyclohexane are sharp and show that two *trans* isomers are present in solution in addition to the *cis* isomer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the molybdenum carbene 24 at room temperature are consistent with its existence as a mixture of *cis* and *trans* isomers. In CDCl<sub>3</sub> the *cis*: *trans* ratio is 53:47. In  $[^{2}H_{6}]$  acetone this ratio is 37:63. The population of the *cis* isomer 23.

Two *trans* species are evident in the IR and variabletemperature <sup>1</sup>H NMR spectra. Unlike the tungsten case, there is no indication of a third *trans* isomer in the IR spectrum of complex 24 in  $C_6H_{12}$ . Only one *cis* isomer is seen by IR and

Table 5 Atom coordinates (  $\times\,10^4$  ) for [WI(CO)\_{2}=C(OEt)Ph}(\eta-C\_{5}H\_{5})] 23

	Atom	x	у	Z
,	W	223(1)	2048(1)	2144(1)
]	I	-2179(2)	3002(2)	2841(2)
	O(1)	-711(23)	471(14)	3636(15)
	O(2)	1561(25)	3902(16)	3394(16)
	O(3)	3046(20)	1070(15)	1971(14)
	C(1)	-305(26)	1062(21)	3162(15)
(	C(2)	1035(29)	3252(20)	2960(18)
(	C(3)	63(23)	2853(13)	590(15)
(	C(4)	-1306(23)	2398(13)	648(15)
	C(5)	-1107(23)	1319(13)	747(15)
	C(6)	385(23)	1106(13)	749(15)
	C(7)	1107(23)	2054(13)	652(15)
	C(8)	2247(26)	1463(12)	2591(18)
	C(9)	2949(18)	1450(11)	3670(11)
	C(10)	3925(18)	2241(11)	3960(11)
	C(11)	4687(18)	2250(11)	4921(11)
	C(12)	4472(18)	1468(11)	5591(11)
	C(13)	3495(18)	677(11)	5301(11)
	C(14)	2734(18)	668(11)	4340(11)
	C(15)	4383(32)	544(18)	2294(25)
	C(16)	4852(34)	148(28)	1369(26)

Table 6 Bond lengths (Å) and angles (°) with e.s.d.s for  $[WI(CO)_2-\{=C(OEt)Ph\}(\eta-C_5H_5)]$  23

	2.834(9) 2.005(26) 2.357(21) 2.272(21) 2.052(24) 1.106(33) 1.517(28) 1.473(50) 1.420	W-C(1) W-C(3) W-C(5) W-C(7) O(1)-C(1) O(3)-C(8) O(3)-C(15) C-C(phenyl)	1.992(25) 2.334(21) 2.319(20) 2.281(23) 1.100(32) 1.301(32) 1.439(34) 1.395
$\begin{array}{l} I-W-C(1)\\ C(1)-W-C(2)\\ C(1)-W-C(8)\\ W-C(1)-O(1)\\ O(3)-C(15)-C(16)\\ W-C(8)-O(3)\\ O(3)-C(8)-C(9)\\ C(8)-C(9)-C(14)\\ C-C-C(\eta-C_5H_5) \end{array}$	76.7(8) 103.4(10) 82.0(10) 171.7(19) 104.6(24) 122.8(17) 113.9(19) 123.5(9) 108.0	I-W-C(2) I-W-C(8) C(2)-W-C(8) W-C(2)-O(2) C(8)-O(3)-C(15) W-C(8)-C(9) C(8)-C(9)-C(10) C-C-C(phenyl)	74.5(8) 143.4(7) 82.1(9) 175.8(24) 122.7(21) 123.3(16) 116.4(9) 120.0

variable-temperature <sup>1</sup>H NMR spectroscopy. At -80 °C in [<sup>2</sup>H<sub>6</sub>]acetone, signals at  $\delta_{\rm H}$  5.37 and 5.75 in the ratio 60:40 are assigned to the C<sub>5</sub>H<sub>5</sub> functions of two *trans* isomers. These are exchange broadened by about 11 Hz. Activation-energy values of around 41 kJ mol<sup>-1</sup> are obtained from these spectra. The process associated with this barrier is probably the same as that in the analogous tungsten complex **23**. Satisfactory <sup>13</sup>C NMR spectra are not obtained at -80 °C. The signals expected for the *trans* species are not seen. The resonances are apparently collapsed into the baseline by exchange broadening. A high-temperature-limit <sup>13</sup>C NMR spectrum can be recorded at room temperature and the data are in Table 2.

Addition of  $I_2$  to *trans*-[Mo(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] 5 at -80 °C, followed by warming to room temperature, results in a deep orange solution. On work-up, two crops of crystals are obtained. The expected carbene [MoI(CO)<sub>2</sub>{=C-(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] 25 is isolated in 33% yield as a first crop. The <sup>1</sup>H and <sup>13</sup>C NMR spectra show it exists as one *trans* isomer. The second crop is a mixture of 25 and 24. The mechanism of formation of 24 in this reaction is not yet understood. A related phenyl-exchange reaction takes place when the tungsten complex 6 is treated with I<sub>2</sub>. In this case, the phenyl carbene 23 is the major product (45%) while the desired 26 is the minor product (based on the masses of the mixtures isolated and <sup>1</sup>H NMR integrals in the spectrum of the mixture). Although the initially crystallized material contains only 14% of **26** an analytically pure sample is formed by repeated fractional crystallisation.

Addition of I<sub>2</sub> to  $[Mo(SnPh_3)(CO)_2 = C(OEt)Ph \{(\eta - C_5Me_5)]$  17 at -60 °C produces a deep red solution. The IR spectrum shows the replacement of the bands of the starting material with two new bands  $[v_{CO}(CH_2Cl_2)$ : 1945s and 1865m cm<sup>-1</sup>] whose intensities are characteristic of a *cis*-dicarbonyl. Comparison with the IR spectrum of *cis*- $[MoI(CO)_2 = C - (OEt)Ph \{(\eta - C_5H_5)] [v_{CO}(CH_2Cl_2)$ : 1957s and 1879m cm<sup>-1</sup>]<sup>2</sup> strongly suggests the product is *cis*- $[MoI(CO)_2 = C - (OEt)Ph \{(\eta - C_5H_5)] [v_{CO}(CH_2Cl_2)$ : 1957s and 1879m cm<sup>-1</sup>]<sup>2</sup> strongly suggests the product is *cis*- $[MoI(CO)_2 = C - (OEt)Ph \{(\eta - C_5Me_5)]$  27 and that it forms cleanly. However, attempted chromatography of the reaction mixture to remove SnIPh\_3, including at -60 °C on alumina, results in extensive decomposition.

The only product isolated in significant quantity is the yellow, crystalline phenyl [MoPh(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **28** resulting from loss of EtI from the iodocarbene. Traces of the triiodide [MoI<sub>3</sub>(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **29** are also isolable (see below). Complex **28** is fully characterized and appears reasonably stable in the solid state. Notably, attempts to isolate the  $\eta$ -C<sub>5</sub>H<sub>5</sub> analogue [MoPh(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] fail. Alkylation of the anion [Mo(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)]<sup>-</sup> with [IPh<sub>2</sub>][BF<sub>4</sub>] produces a mixture of products in which the phenyl group is attached to the  $\eta$ -C<sub>5</sub>H<sub>5</sub> ring.<sup>24</sup> Similarly, attempts to decarbonylate the benzoyl complex [Mo(COPh)(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] to the phenyl complex [MoPh(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] also result in products with the phenyl group bound to the  $\eta$ -C<sub>5</sub>H<sub>5</sub> ligand.<sup>25</sup> Presumably the phenyl complex [MoPh(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] is formed initially but undergoes very rapid phenyl migration from the metal to the  $\eta$ -C<sub>5</sub>H<sub>5</sub> ring. There is no evidence for such behaviour in **28**.

The IR spectrum of complex 29 is very similar to that reported for  $[WI_3(CO)_2(\eta-C_5Me_5)]$   $[v_{CO}(CH_2Cl_2)$ : 2560s and 2004s cm<sup>-1</sup>]<sup>26</sup> supporting its formulation as **29**. We synthesised this complex independently by the reaction of  $[Mo_2(CO)_6(\eta C_5Me_5_2$  with excess of  $I_2$  in toluene and its properties do indeed correspond to the small amount of material isolated in the reaction of 17 with I<sub>2</sub>. Monitoring the IR spectrum of the reaction of complex 18 with  $I_2$  under the same conditions shows that it proceeds less cleanly than in the molybdenum case. Several products are formed. The IR spectrum of one component suggests it is the desired complex 30, but again decomposition occurs on chromatography. A small amount of red-orange crystalline material (6 mg) was isolated. The IR spectrum shows two bands at high frequency  $[v_{CO}(CH_2Cl_2):$ 2049m and 2003s cm<sup>-1</sup>]. The mass spectrum shows the molecular ion  $[M]^+$  at m/z 756 which compares well with the published data for complex 31.26

#### Experimental

Infrared spectra were recorded using a Perkin-Elmer 257 instrument, calibrated using the 1601.4 cm<sup>-1</sup> absorption of polystyrene film, or on a Perkin-Elmer 1700 Fourier-transform instrument linked to a Perkin-Elmer 4600 data station. Proton NMR spectra were recorded using Perkin-Elmer R34 (220 MHz), Bruker AM-250 (250 MHz), or Bruker WH-400 (400 MHz) instruments, <sup>13</sup>C NMR spectra using the Bruker AM-250 (62.9 MHz) spectrometer. Mass spectra were recorded using either Kratos MS25 [electron-impact (EI) mode] or MS80 [fast atom bombardment (FAB) mode] instruments.

All reactions were performed under nitrogen or argon atmospheres using deoxygenated solvents dried with an appropriate agent: tetrahydrofuran (thf) from sodium-benzophenone,  $CH_2Cl_2$  from  $CaH_2$ , and light petroleum (b.p. 40– 60 °C throughout) from LiAlH<sub>4</sub>. All other materials were used as supplied.

Preparations.—SnI(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>. Iodine (2.60 g, 10.2 mmol)

was added in portions to a suspension of  $Sn(C_6H_4Me-4)_4$  (5.0 g, 10.4 mmol) in gently refluxing  $CHCl_3$  (100 cm<sup>3</sup>), allowing the purple colouration to be discharged between additions. The resulting solution was evaporated to dryness and filtered through alumina (10 × 2 cm) in dichloromethane. Removal of the solvent gave a crude product as a beige, oily solid (2.77 g) which was used without further purification. Proton NMR and mass spectrometry evidence indicated that the impurities included unreacted  $Sn(C_6H_4Me-4)_4$  and  $(4-MeC_6H_4)_2$ .

 $[Mo(SnPh_3)(CO)_3(\eta-C_5H_5)]$  1. The following is an improved synthesis of complex 1. In our hands, the literature progave moderate yields (ca. 55%) or impure products cedures 2' (mostly contaminated by SnPh<sub>4</sub> and Sn<sub>2</sub>Ph<sub>6</sub>) requiring extensive purification. The following method was adopted instead. A solution of  $Na(C_{10}H_8)$  (55.8 cm<sup>3</sup>, 0.4 mol dm<sup>-3</sup> in thf, 22.3 mmol) was added to a stirred suspension of  $[Mo_2(CO)_6(\eta C_5H_5_2$  (5.00 g, 10.20 mmol) in thf (150 cm<sup>3</sup>) at -80 °C over 40 min. After addition of solid  $SnIPh_3$  (10.60 g, 22.22 mmol) the brown mixture was allowed to warm to room temperature (30 min). The solvent was removed and the residue extracted with  $CH_2Cl_2$  (300 cm<sup>3</sup>). After filtration through  $Al_2O_3$  (6 × 4 cm), the CH<sub>2</sub>Cl<sub>2</sub> was removed at reduced pressure. Sublimation [0.1 mmHg (ca. 13.3 Pa), 100 °C, 1 h] removed the C<sub>10</sub>H<sub>8</sub> leaving pure  $[Mo(SnPh_3)(CO)_3(\eta-C_5H_5)]$  1 as an off-white solid (11.4 g, 94%).

[W(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **2**. By a similar route to that of the preparation of **1**, the tricarbonyl **2** was synthesised in 81% yield from Na(C<sub>10</sub>H<sub>8</sub>) (41.0 cm<sup>3</sup>, 0.4 mol dm<sup>-3</sup> in thf, 16.4 mmol), [W<sub>2</sub>(CO)<sub>6</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (5.00 g, 7.50 mmol), and SnIPh<sub>3</sub> (7.80 g, 16.35 mmol).

[Mo(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] 7. Addition of LiBu (9.2 cm<sup>3</sup>, 1.4 mol dm<sup>3</sup> in hexane, 12.9 mmol) to a solution of C<sub>5</sub>Me<sub>5</sub>H (2.0 cm<sup>3</sup>, 12.9 mmol) in thf (100 cm<sup>3</sup>) produced a deep yellow suspension. A small excess of [Mo(CO)<sub>6</sub>] (3.6 g, 13.6 mmol) was added and the mixture heated at reflux for 24 h. An IR spectrum [ $v_{CO}$ (thf): 1889s, 1791s and 1709s cm<sup>-1</sup>] indicated formation of the anion [Mo(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)]<sup>-</sup>. Addition of SnIPh<sub>3</sub> (10.1 g, 21.2 mmol) was followed by stirring overnight, and removal of solvent. The product was extracted into light petroleum–dichloromethane (1:1) and filtered through Al<sub>2</sub>O<sub>3</sub> (8 × 2 cm). Recrystallization from light petroleum–dichloromethane gave large yellow crystals of [Mo(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] 7 (4.33 g, 51%).

 $[W(SnPh_3)(CO)_3(\eta-C_5Me_5)]$  8. The tungsten complex  $[W(SnPh_3)(CO)_3(\eta-C_5Me_5)]$  8 was obtained by an analogous route to that for 7. A reduced rate of reaction necessitated a 50 h reflux to form the anion  $[W(CO)_3(\eta-C_5Me_5)]^-$  from  $[W(CO)_6]$  (4.8 g, 13.6 mmol). Subsequent reaction with SnIPh<sub>3</sub> (6.0 g, 12.6 mmol) produced the desired complex 8 in 4 h. After work-up, recrystallization from dichloromethane–light petroleum produced  $[W(SnPh_3)(CO)_3(\eta-C_5Me_5)]$  8 (5.52 g, 57%).

[Mo{Sn(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **15**. The complex [Mo{Sn(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **15** was prepared in a similar way to 7 by treatment of the anion [Mo(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)]<sup>-</sup>, prepared from [Mo(CO)<sub>6</sub>] (1.08 g, 4.08 mmol) as above, with SnI(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub> (2.02 g, 3.9 mmol). Yellow crystals of [Mo{Sn(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] were isolated (1.99 g, 73%).

[W{Sn(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **16**. The complex [W{Sn(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **16** was prepared in a similar way to 7 by treatment of the anion [W(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)]<sup>-</sup>, prepared from [W(CO)<sub>6</sub>] (2.38 g, 6.8 mmol) as above, with SnI(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub> (12.7 g, 24.4 mmol). Yellow crystals of [W{Sn(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] were isolated (2.06 g, 40%).

 $[Mo(SnPh_3)(CO)_3(\eta^5-C_9H_7)]$  9. A solution of LiBu (19.0 cm<sup>3</sup>, 1.3 mol dm<sup>-3</sup> in hexane, 25 mmol) was added to a solution of indene (2.9 g, 25 mmol) in thf (120 cm<sup>3</sup>). Molybdenum hexacarbonyl (6.6 g, 25 mmol) was added to the resulting orange solution and the mixture refluxed for 24 h. After cooling, SnClPh<sub>3</sub> (10.6 g, 27 mmol) was added and the solution stirred

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at room temperature for 2 h. The reaction mixture was then filtered through alumina ( $10 \times 2$  cm) three times, before removing the solvent. Dissolution of the resulting orange oil in light petroleum–dichloromethane, followed by evaporation of the solvent, yielded [Mo(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)] 9 (11.4 g, 71%) as a yellow powder.

 $[W(\text{SnPh}_3)(\text{CO})_3(\eta^5-\text{C}_9\text{H}_7)]$  **10**. A similar procedure to that of complex **9** but using  $[W(\text{CO})_6]$  (8.8 g, 25 mmol) gave  $[W(\text{SnPh}_3)(\text{CO})_3(\eta^5-\text{C}_9\text{H}_7)]$  **10** (10.7 g, 59%) as yellow crystals.

 $[Mo(SnPh_3)(CO)_2 = C(OEt)Ph (\eta - C_5H_5)]$  3. A solution of LiPh (4.2 cm<sup>3</sup>, 0.4 mol dm<sup>-3</sup> in  $Et_2O$ , 1.7 mmol) was added to a stirred suspension of  $[Mo(SnPh_3)(CO)_3(\eta-C_5H_5)]$  1 (1.00 g, 1.68 mmol) in  $Et_2O$  (25 cm<sup>3</sup>) at room temperature. The tricarbonyl dissolved to give a yellow solution; sometimes a green intermediate colour was observed. After stirring (15 min) a yellow powder, trans-Li[Mo(COPh)(SnPh<sub>3</sub>)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)], precipitated. The solvent was removed at reduced pressure and the residue dissolved in water  $(30 \text{ cm}^3)$ . Solid [OEt<sub>3</sub>][BF<sub>4</sub>] was added in small portions until the reaction mixture was just acidic. The crude product was extracted into  $CH_2Cl_2$  (50 cm<sup>3</sup>) and the resulting orange solution filtered through  $Al_2O_3$  (5  $\times$  2 cm). The solvent was removed, the residue extracted with light petroleum- $CH_2Cl_2$  (4:1) (50 cm<sup>3</sup>), and the filtration through alumina repeated. Removal of the solvent gave the carbene 3 as an orange powder (1.04 g, 88%). Essentially quantitative yields were obtained on scaling to 10.0 g (16.8 mmol) of the tricarbonyl 1.

[W(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>5</sub>)] **4**. In a similar manner to the preparation of **3**, [W(SnPh<sub>3</sub>)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] **2** (1.00 g, 1.46 mmol) was treated with LiPh (3.7 cm<sup>3</sup>, 0.4 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 1.5 mmol), and [OEt<sub>3</sub>][BF<sub>4</sub>] to form the carbene **4** (0.86 g, 75%). Again, essentially quantitative yields were obtained when the reaction was scaled to 10.0 g (14.6 mmol) of [W(SnPh<sub>3</sub>)(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>)] **2**.

 $[Mo(SnPh_3)(CO)_2 = C(OEt)Ph (\eta - C_5Me_5)]$  17. The complex [Mo(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] 7 (1.00 g, 1.50 mmol) was dissolved in Et<sub>2</sub>O (25 cm<sup>3</sup>) and LiPh (1.8 cm<sup>3</sup>, 1.16 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 2.09 mmol) added whilst stirring at room temperature. The solvent was removed under vacuum to produce an orangeyellow oil. After hydrolysis with iced water (ca. 30 cm<sup>3</sup>), [OEt<sub>3</sub>][BF<sub>4</sub>] was added in portions, until the solution was slightly acidic. Extraction into dichloromethane  $(3 \times 50 \text{ cm}^3)$ produced a deep orange solution which was chromatographed on  $Al_2O_3$  (30 × 1.5 cm) eluting with light petroleumdichloromethane (3:1). Recrystallization of the main orange fraction from hexane-dichloromethane gave the carbene  $[Mo(SnPh_3)(CO)_2 = C(OEt)Ph (\eta - C_5Me_5)]$  17 (0.88 g, 76%). Recrystallization from light petroleum-dichloromethane or hexane-dichloromethane yielded pale orange cubic crystals, whereas deep red needles were obtained from diethyl etherhexane. These represent two different crystal forms, the former containing CH<sub>2</sub>Cl<sub>2</sub> of crystallization. The orange material turns red at 80 °C as the CH2Cl2 of crystallization is driven off and then melts at 157 °C with decomposition.

[W(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Ph}( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **18**. Using the same procedure as that above, the tungsten analogue was prepared. Reaction of [W(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **8** (3.00 g, 3.98 mmol) with LiPh (6.0 cm<sup>3</sup>, 1.16 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 7.44 mmol), followed by alkylation and work-up, gave red-orange crystals of [W(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Ph}( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **18** (1.86 g, 54%).

 $[Mo{Sn(C_6H_4Me-4)_3}(CO)_2{=C(OEt)(C_6H_4Me-4)}(\eta-$ 

C<sub>5</sub>Me<sub>5</sub>)] 21. By adapting the method described above for the synthesis of complex 17,  $[Mo{Sn(C_6H_4Me-4)_3}(CO)_3(\eta-C_5Me_5)]$  15 (0.8 g, 1.13 mmol) was treated with Li(C<sub>6</sub>H<sub>4</sub>Me-4) (3.2 cm<sup>3</sup>, 0.85 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 2.7 mmol) and  $[OEt_3][BF_4]$  to afford  $[Mo{Sn(C_6H_4Me-4)_3}(CO)_2{=C(OEt)(C_6H_4Me-4)}(\eta-C_5Me_5)]$  (0.62 g, 66%).

 $[W{Sn(C_6H_4Me-4)_3}(CO)_2{=C(OEt)(C_6H_4Me-4)}(\eta-C_5Me_5)]$  22. By adapting the method described above for the synthesis of complex 17,  $[W{Sn(C_6H_4Me-4)_3}(CO)_3(\eta-C_5Me_5)]$ 

C<sub>5</sub>Me<sub>5</sub>)] 16 (0.90 g, 1.13 mmol) was treated with Li(C<sub>6</sub>H<sub>4</sub>Me-4) (7.0 cm<sup>3</sup>, 0.85 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 5.95 mmol) and [OEt<sub>3</sub>][BF<sub>4</sub>] to afford [W{Sn(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(CO)<sub>2</sub>{=C(OEt)-(C<sub>6</sub>H<sub>4</sub>Me-4)}( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] (0.60 g, 58%).

 $[C_6H_4Me-4]{(\eta-C_5Me_5)]}(0.60 g, 58\%).$   $[Mo(SnPh_3)(CO)_2{=C(OEt)Ph}{(\eta^5-C_9H_7)]}$  19. A solution of  $[Mo(SnPh_3)(CO)_3(\eta^5-C_9H_7)]$  9 (5.0 g, 7.7 mmol) in Et<sub>2</sub>O (20 cm<sup>3</sup>) was treated with LiPh (8.2 cm<sup>3</sup>, 1.22 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 10 mmol). After stirring at room temperature (20 min), the solvent was removed and the reaction mixture alkylated using  $[OEt_3]$ -  $[BF_4]$ , as described above. Extraction into dichloromethane (3 × 40 cm<sup>3</sup>) and filtration through alumina (8 × 2 cm<sup>3</sup>) gave an orange solution. Recrystallization from dichloromethane-hexane yielded orange microcrystalline  $[Mo(SnPh_3)-(CO)_2{=C(OEt)Ph}(\eta^5-C_9H_7)]$  19 (4.70 g, 81%).

 $[W(SnPh_3)(CO)_2\{=C(OEt)Ph\}(\eta^5-C_9H_7)]$  20. The complex  $[W(SnPh_3)(CO)_2\{=C(OEt)Ph\}(\eta^5-C_9H_7)]$  20 (2.82 g, 49%) was obtained by modifying the synthesis of 19 to use  $[W(SnPh_3)-(CO)_3(\eta^5-C_9H_7)]$  10 (5.0 g, 6.8 mmol) and LiPh (7.2 cm<sup>3</sup>, 1.22 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 8.8 mmol).

[Mo(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **5**. Impure trans-[Mo(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **5** was obtained by adapting the synthesis of **3**, but starting from LiMe (2.0 cm<sup>3</sup>, 1.75 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 3.5 mmol) and [Mo(SnPh<sub>3</sub>)(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **1** (1.00 g, 1.68 mmol). Chromatography on Al<sub>2</sub>O<sub>3</sub> (10 × 2 cm) in light petroleum–CH<sub>2</sub>Cl<sub>2</sub> (3:1) gave a colourless mixture of uncharacterized materials, followed by the pure yellow carbene **5**. Crystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexane gave pure **5** as a yellow solid (0.79 g, 74%).

[W(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] 6. Impure [W-(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] 6 was obtained by modifying the synthetic procedure for 3, but starting from LiMe (5.8 cm<sup>3</sup>, 1.75 mol dm<sup>-3</sup> in Et<sub>2</sub>O, 10.2 mmol) and the tin complex 2 (1.00 g, 1.46 mmol). Chromatography on Al<sub>2</sub>O<sub>3</sub> (10 × 2 cm) in light petroleum–CH<sub>2</sub>Cl<sub>2</sub> (3:1) gave a colourless mixture of uncharacterized materials, followed by a yellow fraction containing the carbene 6. Compound 6 was isolated pure from CH<sub>2</sub>Cl<sub>2</sub>-hexane as a yellow powder (0.73 g, 69%).

[MoI(CO)<sub>2</sub>{=C(OEt)Ph}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **24**. Solid I<sub>2</sub> (1.98 g, 7.80 mmol) was added to a cold (-80 °C) solution of *trans*-[Mo(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Ph}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **3** (5.47 g, 7.80 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>). As the mixture warmed to room temperature (2 h) it became very dark. The solvent was removed and the residue chromatographed on Al<sub>2</sub>O<sub>3</sub> (16 × 4 cm) at -80 °C. Elution with light petroleum–CH<sub>2</sub>Cl<sub>2</sub> (1:1) afforded a dark orange band, while the SnIPh<sub>3</sub> by-product was strongly retained on the column. Crystallization of the dark fraction yielded **24** as maroon microcrystalline needles (2.42 g, 65%).

 $[WI(CO)_2{=C(OEt)Ph}(\eta-C_5H_5)]$  23. By following the above method for the synthesis of complex 24, but using I<sub>2</sub> (1.77 g, 6.97 mmol) and the carbene 4 (5.50 g, 6.97 mmol), the carbene 23 was obtained as red crystals (3.11 g, 79%).

 $[MoI(CO)_2 = C(OEt)Ph (\eta - C_5Me_5)]$  27 (attempted). The complex  $[Mo(SnPh_3)(CO)_2 = C(OEt)Ph (\eta - C_5Me_5)]$  17 (0.5 g, 0.65 mmol) was treated with  $I_2$  (0.16 g, 0.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub>  $(15 \text{ cm}^3)$  at  $-78 \text{ }^\circ\text{C}$  and warmed to ambient temperature. After 30 min the mixture was rapidly filtered through alumina  $(10 \times 1.5 \text{ cm})$  at  $-60 \text{ }^{\circ}\text{C}$  to produce a dark maroon solution. Recrystallization from dichloromethane-hexane yielded a dark purple, oily solid (0.19 g). Mass spectrometry (FAB) confirmed the presence of the iodocarbene cis- $[MoI(CO)_2 = C(OEt)Ph](\eta$ - $C_5Me_5$ ] 27, with peaks assignable to successive carbonyl and iodide loss. The <sup>1</sup>H NMR spectrum, however, indicated the presence of impurities including SnIPh<sub>3</sub>. Attempts to purify 27 by chromatography resulted in extensive decomposition, even at -60 °C. The major decomposition product was the new aryl complex [MoPh(CO)<sub>3</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] 28, isolated in yields of up to 50%. Small amounts of  $[MoI_3(CO)_2(\eta-C_5Me_5)]$  29 (comparison of IR and mass spectra with those of an authentic sample) were also obtained.

 $[WI(CO)_2{=C(OEt)Ph}(\eta-C_5Me_5)]$  30 (attempted). The reaction between  $[W(SnPh_3)(CO)_2{=C(OEt)Ph}(\eta-C_5Me_5)]$ 

18 (0.50 g, 0.58 mmol) and I<sub>2</sub> (0.15 g, 0.58 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was executed as in the attempted preparation of complex 27. The IR spectrum suggests a mixture of complex 30  $[v_{CO}(CH_2Cl_2):$  1939s and 1855m cm<sup>-1</sup>] and starting material. However, repeated attempts to separate these complexes using chromatography on alumina at -78 °C were unsuccessful. The other product of the reaction was isolable in trace amounts and was identified as  $[WI_3(CO)_2(\eta-C_5Me_5)]$  31 by mass and infrared spectroscopy. Addition of excess of I<sub>2</sub> to the reaction, in

increasing amounts of the required iodocarbene **30**. [MoI(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **25**. Using a similar method to that for the synthesis of complex **24**, but using I<sub>2</sub> (0.20 g, 0.78 mmol) and [Mo(SnPh<sub>3</sub>)(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **5** (0.50 g, 0.78 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) gave two crops of orange microcrystals. The first crop was pure [MoI(CO)<sub>2</sub>-{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **25** (0.11 g, 33%). A second crop (54 mg) was a mixture of [MoI(CO)<sub>2</sub>{=C(OEt)Ph}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **24** and **25** in a 69:31 ratio (<sup>1</sup>H NMR spectroscopy).

order to try and consume all the starting material, resulted in an

increased proportion of the triiodo complex 31 rather than

[WI(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **26**. By using a similar method to the synthesis of complex **24**, but starting from I<sub>2</sub> (0.17 g, 0.69 mmol) and the carbene **6** (0.50 g, 0.69 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>), two crops of crystals were obtained. The first crop (0.11 g) was red and consisted of a mixture (by <sup>1</sup>H NMR spectroscopy) of [WI(CO)<sub>2</sub>{=C(OEt)Ph}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **23** and [WI(CO)<sub>2</sub>{=C(OEt)Me}( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] **26** in the ratio 95:5 (<sup>1</sup>H NMR spectrum integrals). The second crop was orange (0.11 g) and contained **23** and **26** in a 61:39 ratio. Total yields, based on the ratios and masses above, were 45% **23** and 14% **26**. A small sample of **26** was obtained pure by repeated fractional crystallization.

[MoI<sub>3</sub>(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **29**. A solution of I<sub>2</sub> (0.51 g, 2.0 mmol) in toluene (30 cm<sup>3</sup>) was added (30 min) to a solution of [Mo<sub>2</sub>(CO)<sub>6</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (0.4 g, 0.63 mmol) in toluene (30 cm<sup>3</sup>) and the solution stirred for 90 min while employing a nitrogen purge. After 72 h in the dark at ambient temperature the complex [MoI<sub>3</sub>(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)] **29** crystallized direct from the reaction mixture as very dark purple microcrystals (0.67 g, 80%).

Crystal Structure Determinations.—General considerations for both structures. Three-dimensional, room-temperature Xray data were collected in the range  $3.5 < 2\theta < 50^{\circ}$  on a Nicolet R3 four-circle diffractometer by the  $\omega$ -scan method. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

[WI(CO)<sub>2</sub>{=C(OEt)Ph}(η-C<sub>5</sub>H<sub>5</sub>)] **23**. C<sub>16</sub>H<sub>15</sub>IO<sub>3</sub>W, M = 566.00, crystallizes from dichloromethane-hexane as red blocks, crystal dimensions 0.30 × 0.25 × 0.15 mm, monoclinic, space group  $P2_1/c$  ( $C_{2h}^{5}$ , no. 14); a = 9.34(3), b = 13.00(2), c = 13.53(3) Å,  $\beta = 97.8(2)^{\circ}$ , U = 1628(7) Å<sup>3</sup>,  $D_c = 2.309$  g cm<sup>-3</sup>, Z = 4; Mo-K<sub>α</sub> radiation ( $\lambda = 0.710$  69 Å),  $\mu$ (Mo-K<sub>α</sub>) = 91.32 cm<sup>-1</sup>, F(000) = 1047.75.

The 2091 independent reflections of 3215 measured for which  $|F|/\sigma(|F|) > 3.0$  were corrected for Lorentz and polarization effects, and for absorption by analysis of eight azimuthal scans (minimum and maximum transmission coefficients of 0.002 and 0.014 respectively). The structure was solved by standard Patterson and Fourier methods. Geometric constraints were imposed on the phenyl (D<sub>6h</sub> symmetry, C-C 1.395 Å) and cyclopentadienyl rings (D<sub>5h</sub> symmetry, C-C 1.420 Å). The two W-C and C-O bond lengths were constrained to be equal, although collinearity of W-C-O was not imposed. The structure was refined by blocked-cascade least squares, with allowance for the thermal anisotropy of all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with isotropic thermal parameters related to the supporting atom. Refinement converged at R 0.0812 (R' = 0.0875, 171 parameters, maximum shift/e.s.d. 0.074). A final difference electron-density synthesis showed peaks of -3.47 and +1.78Å<sup>-3</sup> near to tungsten. Complex scattering factors were taken from the SHELXTL<sup>28</sup> computing package which was used for the structure refinement and from ref. 29. The weighting scheme

was  $w = [\sigma^2(F) + gF^2]^{-1}$  with g = 0.002.  $[Mo(SnPh_3)(CO)_2 = C(OEt)Ph (\eta - C_5Me_5)] \cdot CH_2Cl_2$ 17.  $C_{40}H_{42}Cl_2MoO_3Sn$ , M = 856.30, crystallizes from dichloromethane-hexane as orange blocks, dimensions of two crystals used  $0.275 \times 0.20 \times 0.10$  and  $0.225 \times 0.15 \times 0.075$  mm, monoclinic, space group  $P2_1/n$  (a non-standard setting of  $P2_1/c$ ,  $C_{2h}^{5}$ , no. 14); a = 14.611(36), b = 16.788(20), c = 16.183(30) Å,  $\beta = 96.08(18)^{\circ}$ , U = 3947(13) Å<sup>3</sup>,  $D_{c} = 1.441$  g cm<sup>-3</sup>, Z = 4, Mo-K $\alpha$  radiation ( $\lambda = 0.710$  69 Å),  $\mu$ (Mo-K $\alpha$ ) = 11.14 cm<sup>-1</sup>, F(000) = 1727.67.

The 2117 independent reflections (of 7539 measured, including a number of duplicates for scaling purposes) for which  $[F|/\sigma(|F|) > 5.0$  were recorded from two crystals, which decayed over a period of a few days: all data used were acquired before intensity loss had exceeded 50%, and were corrected for this decay and mutually scaled ( $R_{merge} = 0.048$ ). All data were corrected for Lorentz and polarization effects, but no correction was made for absorption. The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade leastsquares methods. The dichloromethane of solvation was found to be disordered (refined occupancy parameters 0.66, 0.34) in two interpenetrating sites: its geometry was optimized and each component was refined as a rigid group. Geometric constraints were also applied to the phenyl  $(D_{6h})$  and cyclopentadienyl  $(D_{5h})$  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 0.0888 (172 parameters, maximum shift/e.s.d. 0.001), with allowance for the thermal anisotropy of the tin, molybdenum, oxygen and high-occupancy chlorine atoms only. A final difference electron-density synthesis showed peaks of -0.86 and +1.65 e Å<sup>-3</sup>. Complex scattering factors were taken from the program package SHELXTL<sup>28</sup> as implemented on the Data General Nova 3 computer, which was used for structure solution and refinement. Unit weights were used throughout the refinement.

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