

## Indenyl and fluorenyl transition metal complexes

### XV \*. Reactions of 1,1-dimethylindene, spirocyclopropane-1,1-indene, and spirocyclopropane-9,9-fluorene with $L_3M(CO)_3$ (L = $NH_3$ , Py; M = Cr, Mo, W)

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(Received June 6th, 1987)

#### Abstract

Reaction of indene, 1,1-dimethylindene, spirocyclopropane-1,1-indene, and spirocyclopropane-9,9-fluorene with  $Py_3M(CO)_3/BF_3 \cdot OEt_2$  (M = Cr, Mo, W) involves two competing processes: (i) the formation of the  $\eta^6$ -arene complexes (**A**) and (ii) the oxidative addition at the C(1)–R and C(9)–R bonds (R = alkyl) with the formation of chelated  $\sigma, \pi$ -complex (**B**). The reaction pathway (**A** or **B**) is determined both by the metal and the ligand.

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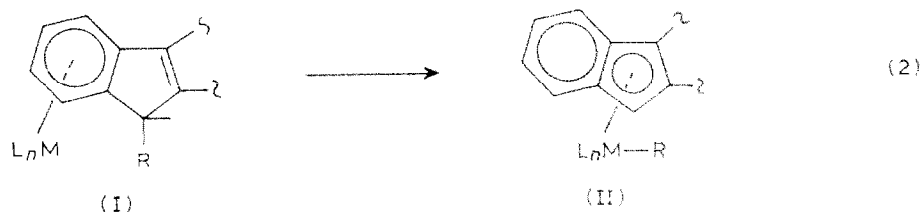
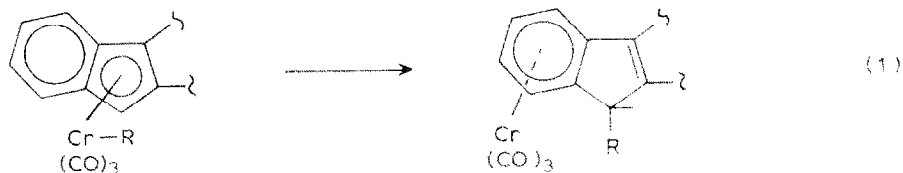
#### Introduction

Inter-ring haptotropic rearrangements of transition metal complexes with polycyclic aromatic ligands have lately been widely investigated [1,2], for instance rearrangements in the naphthalene complexes [3–8] as well as the reversible or irreversible migration of metal atom between the six- and five-membered rings in the indenyl and fluorenyl complexes [9–13], and also in some other systems [14–16]. Those haptotropic rearrangements, in which the migrating metal contains  $\sigma$ -bonded group and its inter-ring motion is accompanied by the transfer of the  $\sigma$ -bonded group between the metal atom and the organic ligand are of considerable interest.

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\* For part XIV see Ref. 27.

We have found such "ricochet" reactions occur in the case of  $\eta^5$ -fluorenyl and  $\eta^5$ -indenyl complexes of chromium [17] (eq. 1). The process proceeds irreversibly and stereospecifically (the alkyl radical is located in the *endo* position with respect to the metal in the  $\eta^6$ -complex):



( R = H , CH<sub>3</sub> , CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> )

There are no reliable data in the literature for "retro-ricochet" rearrangements which are the reverse of eq. 1, and are followed by rupture of the substituent-ligand bond with the migration of the former to the metal (eq. 2). From a formal viewpoint, reaction 2 is an oxidative addition across the C-R bond. Processes of the type shown in eq. 2, both reversible and irreversible, are of interest with respect to the catalytic system which can activate carbon-carbon bonds.

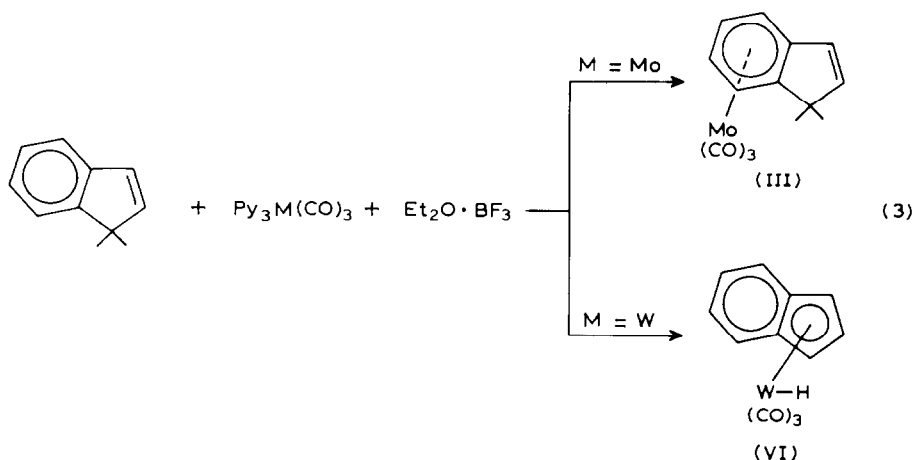
Reaction of  $\text{Py}_3\text{M}(\text{CO})_3/\text{Et}_2\text{O} \cdot \text{BF}_3$  with fluorenes and indenenes substituted in positions 1 and 9, respectively, shows promise as a route to complexes which can undergo conversion 2, because they can form the isomers I and II. The difference in thermodynamic stability between I and II can be reduced using various combinations of substituents with various metals.

In the present work we report on reactions of 1,1-dimethylindene, spirocyclopropane-(1,1)-indene, and spirocyclopropane-(9,9)-fluorene with  $\text{Py}_3\text{M}(\text{CO})_3/\text{Et}_2\text{O} \cdot \text{BF}_3$  and on the reaction of indene with  $\text{Py}_3\text{Cr}(\text{CO})_3/\text{Et}_2\text{O} \cdot \text{BF}_3$ .

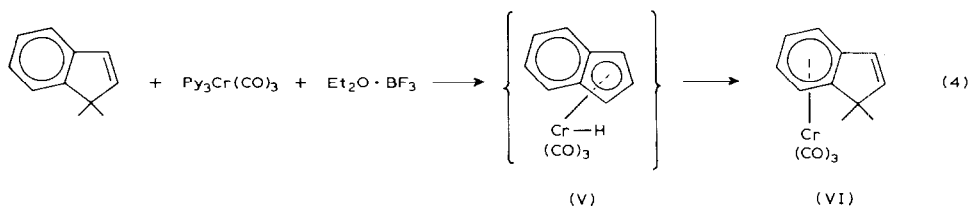
## Results and discussion

We have previously shown [18] that the outcome of indene reaction with  $\text{Py}_3\text{M}(\text{CO})_3/\text{Et}_2\text{O} \cdot \text{BF}_3$  depends on the metal. Thus, when  $\text{M} = \text{Mo}$  the  $\eta^6$ -arene complex III is formed as the final product, whereas with  $\text{M} = \text{W}$  the isomeric hydrido- $\eta^5$ -indenyl complex IV was obtained (eq. 3).

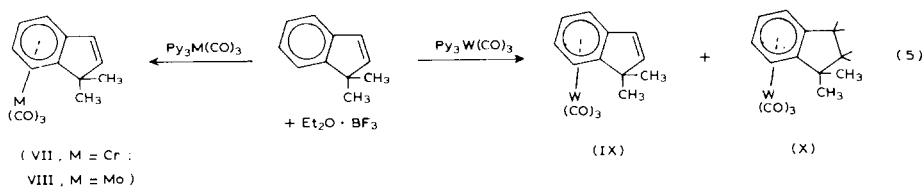
We have found that the reaction of indene with  $\text{Py}_3\text{Cr}(\text{CO})_3$  gives the hydrido- $\eta^5$ -indenyl chromium complex V as the kinetically controlled product, which is subsequently converted to VI at the expense of "ricochet" haptotropic isomerization (eq. 4). The formation of intermediate V was revealed by monitoring



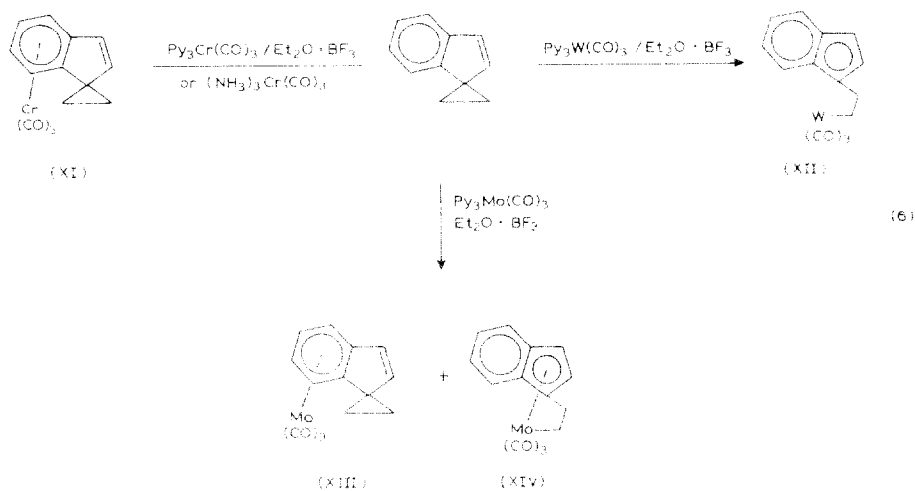
the IR spectra in the very initial stages of the reaction. In an analogous reaction with  $\text{Py}_3\text{W}(\text{CO})_3$ , the hydrido- $\eta^5$ -indenyl complex VI is formed immediately and is the result of both kinetic and thermodynamic control. Hence it follows that in reactions 3 and 4, the rate of indene oxidative addition across the C(1)-H bond to the coordinatively unsaturated “ $\text{M}(\text{CO})_3$ ” fragment is higher than the rate of coordination of indene with the same fragment through the arene ring.



In light of the fact that oxidative addition across the C-C bond is not so as easy as at the C-H bond, we studied the reactions of 1,1-dimethylindene with  $\text{Py}_3\text{M}(\text{CO})_3$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ), and under the same conditions  $\eta^6$ -arene complexes VII-IX were found to have formed in all three cases (eq. 5).



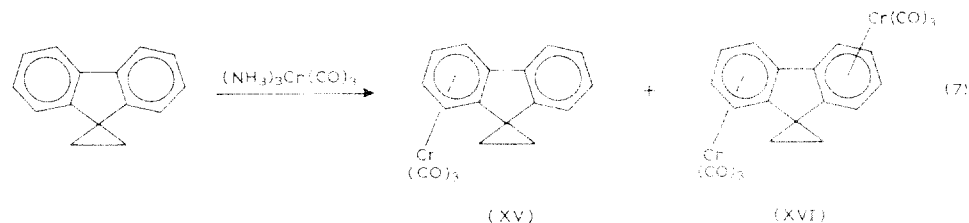
However in the case of  $\text{M} = \text{W}$ , the hydrogenated complex X is formed along with IX. The ratio of complexes IX and X in the mixture was determined by  $^1\text{H}$  NMR and mass spectrometry, because attempts to separate these complexes on silica gel failed. Partial or complete hydrogenation of this type in the presence of Lewis acids was demonstrated in the synthesis of iron [19] and manganese [20] complexes with fused aromatic ligands.



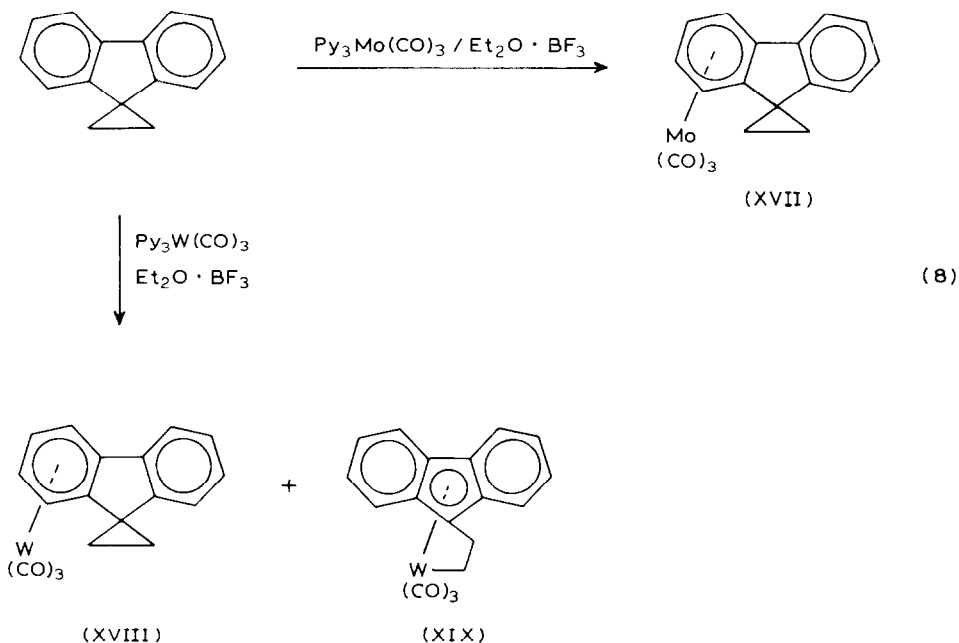
The formation of only  $\eta^6$ -arene complexes in reaction 5 implies that the rate of oxidative addition of 1,1-dimethylindene across the C(1)-CH<sub>3</sub> bond to the "M(CO)<sub>3</sub>" fragment is much less than that of coordination through the arene ring.

It is assumed that the ability of cyclopropane-1,1-indene and spirocyclopropane-9,9-fluorene to undergo oxidative addition to the "M(CO)<sub>3</sub>" fragment owing to rupture of the three-membered cycle would occupy a position between indene and 1,1-dimethylindene since the carbon-carbon bond in these is weakened at the expense of a small strained cycle. This was substantiated during an investigation of their reactions with  $\text{Py}_3\text{M}(\text{CO})_3/\text{BF}_3 \cdot \text{Et}_2\text{O}$  (M = Cr, Mo, W). For instance, spirocyclopropane-1,1-indene reacts in various ways with  $\text{L}_3\text{M}(\text{CO})_3$  and the result is dependent on the metal. With M = Cr, the only reaction product is the  $\eta^6$ -arene complex XI, with M = W, sufficiently stable chelated complex XII is formed which was isolated pure and was characterized. Reaction with  $(\text{C}_5\text{H}_5\text{N})_3\text{Mo}(\text{CO})_3$ , leads to complexes of both types (XIII and XIV), however, the unstable  $\eta^6$ -arene complex, XIII, could not be isolated and was identified only from characteristic bands in the IR spectra and by chromatography.

Spirocyclopropane-9,9-fluorene reacts with  $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$  to form the mono- and binuclear  $\eta^6$ -complexes XV and XVI:



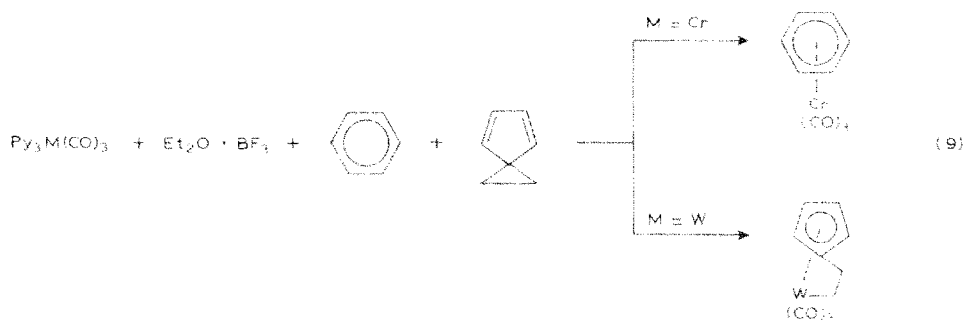
Under Öfele reaction conditions,  $(\text{C}_5\text{H}_5\text{N})_3\text{Mo}(\text{CO})_3$  reacts with spirocyclopropane-9,9-fluorene to give only the  $\eta^6$ -arene complex XVII in 27% yield, and  $(\text{C}_5\text{H}_5\text{N})_3\text{W}(\text{CO})_3$  gives a mixture of the arene complex XVIII and the chelated  $\sigma, \pi$  complex XIX. Complex XVIII was isolated and fully characterized whereas XIX has a low stability and can only be detected by IR spectroscopy.



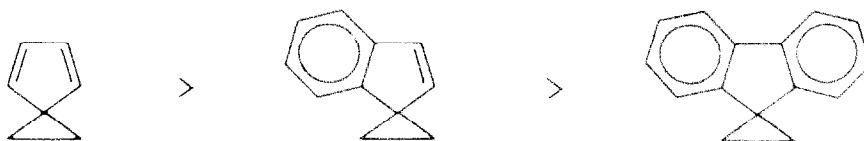
Thus, the C–C bond in the three-membered cycle of spirocyclopropane-1,1-indene and spirocyclopropane-9,9-fluorene is more readily cleaved than the  $\text{CH}_3$ –C bond in 1,1-dimethylindene during oxidative addition to the metal, the ease of scission in spirocyclopropane-1,1-indene being higher than that in spirocyclopropane-9,9-fluorene and the activity of  $\text{L}_3\text{M}(\text{CO})_3$  decreases on going from tungsten to chromium. Such uniformity has previously been reported for reactions of 5,5-dimethyl- and 5,5-diethylcyclopentadienes and spiro-2,4-hepta-4,6-diene with  $\text{L}_3\text{M}(\text{CO})_3$  ( $\text{L}_3 = \text{diglyme}$ ,  $\text{M} = \text{Mo}$ ;  $\text{L} = \text{CH}_3\text{CN}$ ,  $\text{M} = \text{W}$ ) [21].

Of the reactions studied eqs. 5–8, those that are most interesting involve the simultaneous formation of both  $\eta^6$ -arene and  $\sigma, \pi$ -chelated complexes XIII and XIX (eq. 6) or XVIII and XIX (eq. 8). Three ways for the formation of these isomers are possible (i) the isomers are formed independently, (ii) first the  $\sigma, \pi$ -chelated complexes XIV and XIX are formed, then undergo “ricochet” haptotropic isomerization (eq. 1) to the  $\eta^6$ -arene complexes XIII and XVIII, (iii) initial formation of the  $\eta^6$ -isomers takes place with the subsequent partial isomerization by “retro-ricochet” type (eq. 2) to the chelated  $\sigma, \pi$ -isomers. We propose that  $\eta^6$ -arene and chelate  $\sigma, \pi$ -complexes are formed independently, and that the nature of the metal atom determines which isomer should predominate. This was confirmed by the reaction of  $\text{Py}_3\text{M}(\text{CO})_3/\text{BF}_3 \cdot \text{OEt}_2$  ( $\text{M} = \text{Cr}, \text{W}$ ) with a mixture of benzene and spiro-2,4-hepta-4,6-diene (eq. 9).

Results of reaction 9 involving competition by benzene and spiro-2,4-hepta-4,6-diene demonstrate that in the case of  $\text{M} = \text{Cr}$  the arene coordination process is more rapid, whereas with  $\text{M} = \text{W}$  oxidative cleavage of the three-membered cycle predominates. These results are consistent with the exclusive formation of arene complexes in reactions of “ $\text{Cr}(\text{CO})_3$ ” with spirocyclopropane-1,1-indene and spirocyclopropane-9,9-fluorene on one hand, and also consistent with the formation of

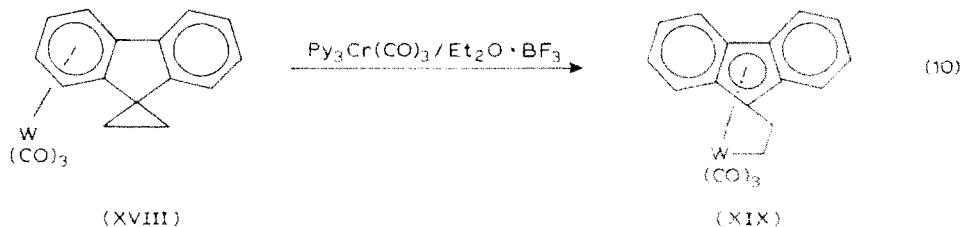


chelated structures for the “W(CO)<sub>3</sub>” fragment, on the other. The reaction is affected to a great extent by the composition of the aromatic ligand bearing the cyclopropane fragment. As noted above the ability for oxidative cleavage of the cyclopropane ring falls in the order:



The simultaneous formation of both isomeric complexes of molybdenum (eq. 6) confirms that the “Mo(CO)<sub>3</sub>” moiety occupies an intermediate place between “Cr(CO)<sub>3</sub>” and “W(CO)<sub>3</sub>”, because of its ability to bring about oxidative cleavage at the three-membered cycle.

At this stage it is difficult to draw decisive conclusions about the reality of pathways (ii) and (iii) in the reactions investigated. Special experiments did not enable us to detect conversions XIII → XIV and XVIII → XIX. Low thermal stability of these complexes led only to the decomposition of the starting  $\sigma, \pi$ -isomers. The same result was obtained when a “retro-ricochet” rearrangement of the type 2 was attempted by heating the  $\eta^6$ -arene complexes XI, XV and XVII. In this case the kinetic barrier for the conversions  $\eta^6 \rightarrow \eta^5$  and  $\eta^6 \rightarrow \eta^5$  is sufficiently high. An attempt to promote the  $\eta^6 \rightarrow \eta^5$  conversion of complex XVIII by the action of  $\text{Py}_3\text{Cr}(\text{CO})_3/\text{BF}_3 \cdot \text{OEt}_2$  resulted in an isomerization product XIX which only was isolated in negligible quantity and was identified from its IR spectrum (eq. 10). The addition of “Cr(CO)<sub>3</sub>” apparently facilitates rupture of the three-membered cycle in the first step of the reaction.



## Experimental

All operations, except for preparative TLC, were carried out under argon. Tetrahydrofuran and dibutyl ether were purified by refluxing over K/Na alloy and over Na, respectively. Ether was refluxed over sodium benzophenone ketyl. All solvents were distilled directly before use. Column chromatography was carried out on silica gel 40/100  $\mu$  (Chemapol, Czechoslovakia) deoxygenated by heating at 170 °C (0.1 mmHg) and stored under argon. Starting compounds were prepared by published procedures: 1,1-dimethylindene [22], spiro-2,4-hepta-4,6-diene [23], spirocyclopropane-9,9-fluorene [24],  $\text{Py}_3\text{M}(\text{CO})_3$  (M = Cr, Mo, W) [25],  $(\text{NH}_3)_3\text{-Cr}(\text{CO})_3$  [26].

$^1\text{H}$  NMR spectra were recorded on a Varian XL-100 spectrometer relative to tetramethylsilane. IR spectra were obtained on a Specord-75 IR instrument.

### *Reactions of substituted indenenes and fluorenes with $\text{Py}_3\text{M}(\text{CO})_3/\text{Et}_2\text{O} \cdot \text{BF}_3$*

1. *1,1-Dimethylindene and  $\text{Py}_3\text{Cr}(\text{CO})_3$* . A mixture of 2 g of  $\text{Py}_3\text{Cr}(\text{CO})_3$  (5.4 mmol) and 0.93 g (6.4 mmol) of 1,1-dimethylindene in 100 ml of ether was stirred with 3.45 ml of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  for 1 h at  $-10^\circ\text{C}$  for 0.5 h and at  $25^\circ\text{C}$ . After the mixture had been diluted with hexane (ca. 30 ml) and decomposed with water, the organic layer was separated, dried over  $\text{MgSO}_4$  and evaporated in vacuo. The residue was chromatographed on  $\text{SiO}_2$  (a column  $3 \times 15$  cm) to yield 0.43 g (31%) of VII, yellow crystals, m.p.  $131\text{--}132^\circ\text{C}$ .

$\nu(\text{CO})$  ( $\text{CHCl}_3$ ) 1900,  $1976\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$  in ppm) 0.8 (s, 3H, *exo*- $\text{CH}_3$ ), 1.18 (s, 3H, *endo*- $\text{CH}_3$ ), 4.22 (t, 1H, H(6),  $J(\text{H}(6),\text{H}(7)) = J(\text{H}(6),\text{H}(5)) = 6$  Hz), 4.68 (m, 2H, H(4) + H(5)), 5.04 (d, 1H, H(7),  $J(\text{H}(7),\text{H}(6)) 6$  Hz), 5.9 (m, 2H, H(2) + H(3)). Found: C, 60.78; H, 4.59; Cr, 18.50.  $\text{C}_{14}\text{H}_{12}\text{CrO}_3$  calc: C, 60.22, H, 4.33; Cr, 18.62%.

2. *1,1-Dimethylindene and  $\text{Py}_3\text{Mo}(\text{CO})_3$* . A mixture of 4 g (9.6 mmol) of  $\text{Py}_3\text{Mo}(\text{CO})_3$ , 1.8 g (12.5 mmol) of 1,1-dimethylindene and 6.1 ml (43.2 mmol) of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  in 120 ml of ether was stirred for 40 min, then diluted with 40 ml of heptane and decomposed with water. The organic layer was separated, and after the ether had been removed in vacuo, cooled in a Dewar flask with dry ice. Yellow crystals of VIII precipitated. These were repeatedly recrystallized with heptane from benzene, yield 0.93 g (30%) m.p.  $146\text{--}147^\circ\text{C}$ .

$\nu(\text{CO})$  ( $\text{Et}_2\text{O}$ ) 1900,  $1980\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) 0.8 (s, 3H, *exo*- $\text{CH}_3$ ), 1.08 (s, 3H, *endo*- $\text{CH}_3$ ), 4.5 (t, 1H, H(6),  $J(\text{H}(6),\text{H}(5)) = J(\text{H}(6),\text{H}(7)) = 6$  Hz), 4.9 (m, 2H, H(4) + H(5)), 5.2 (d, 1H, H(7),  $J(\text{H}(7),\text{H}(6)) 6$  Hz), 5.78 (m, 2H, H(2) + H(3)). Found: C, 52.22; H, 3.77; Mo, 29.22.  $\text{C}_{14}\text{H}_{12}\text{MoO}_3$  calc: C, 52.04; H, 3.74; Mo, 29.68%.

3. *1,1-Dimethylindene and  $\text{Py}_3\text{W}(\text{CO})_3$* . A mixture of 2 g (3.96 mmol) of  $\text{Py}_3\text{W}(\text{CO})_3$  and 0.69 g (4.75 mmol) of 1,1-dimethylindene in 45 ml of dibutyl ether was heated to  $67\text{--}69^\circ\text{C}$ . To the stirred mixture was added 2.53 g (17.8 mmol) of  $\text{Et}_2\text{O} \cdot \text{BF}_3$ , and after stirring for 1 h the mixture was cooled, diluted with heptane and decomposed with water. The organic layer was separated, the solvent was removed in vacuo, and the residue chromatographed on a  $\text{SiO}_2$  column. The yellow band containing the mixture of IX and X was eluted with a mixture of petroleum ether and benzene (1/1), the total yield of IX and X was 0.05 g (3%), the ratio of IX/X  $\approx 0.15$ .  $\nu(\text{CO})$  ( $\text{CHCl}_3$ ) 1890,  $1968\text{ cm}^{-1}$ .

4. *Spirocyclopropane-1,1-indene and  $\text{Py}_3\text{Cr}(\text{CO})_3$* . This run was carried out as described in exp. 1. The reaction of 2 g (5.7 mmol) of  $\text{Py}_3\text{Cr}(\text{CO})_3$  with 0.93 g (6.7 mmol) of spirocyclopropane-1,1-indene and 3.45 g (24.3 mmol) of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  in 100 ml of ether gave 0.09 g (6%) of XI, m.p. 105 °C. For a characterization of XI see exp. 9.

5. *Spirocyclopropane-1,1-indene and  $\text{Py}_3\text{Mo}(\text{CO})_3$* . The reaction was carried out as described in exp. 2. The hexane solution, obtained on treatment of the reaction mixture with 4.14 g (9.9 mmol) of  $\text{Py}_3\text{Mo}(\text{CO})_3$ , 1.5 g (10.7 mmol) of spirocyclopropane-1,1-indene, 6.3 ml (44.7 mmol) of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  and 160 ml of ether, was chromatographed on a Florisil column (Merck,  $3 \times 30$  cm). The red band of most labile  $\sigma, \pi$ -chelated complex XIV was eluted with hexane. Low temperature crystallization from hexane gave 0.2 g (6%) of XIV as orange-red crystals, m.p. 70–71 °C.  $\nu(\text{CO})$ (pentane) 1930, 1957 and 2022  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ) 6.96 (m, 4H, six-membered ring), AB spectrum:  $\delta_A$  4.70 (1H) and  $\delta_B$  5.12 (1H, H(2), H(3))p  $J(\text{H}_2, \text{H}_3)$  2 Hz), 2.78 (m, 1H) and 3.31 (1H, H(1')), 0.6 (2H, H(1'')). Found: C, 51.55; H, 3.53; Mo, 29.58.  $\text{C}_{14}\text{H}_{10}\text{MoO}_3$  calc: C, 52.53; H, 3.13; Mo, 29.79%.

6. *Spirocyclopropane-1,1-indene and  $\text{Py}_3\text{W}(\text{CO})_3$* . The reaction was carried out as described in exp. 3. A mixture of 1 g (2 mmol) of  $\text{Py}_3\text{W}(\text{CO})_3$ , 0.3 g (2.2 mmol) of spirocyclopropane-1,1-indene and 1.3 ml (9.2 mmol) of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  in 50 ml of dibutyl ether gave, after the residue had been extracted with pentane and low-temperature crystallization, 0.125 g of XII as red-orange crystals, m.p. 98–99 °C.  $\nu(\text{CO})$ (pentane) 1927, 1943 and 2015  $\text{cm}^{-1}$ .  $^1\text{H NMR}$ : 6.56–7.14 (m, 4H, six-membered ring), AB spectrum:  $\delta_A$  4.77 (1H) and  $\delta_B$  5.01 (1H, H(2), H(3)):  $J(\text{H}(2), \text{H}(3))$  2 Hz), 0.06–0.42 (m, 2H, H(1)), 2.78 (m, 1H) and 3.31 (1H, H(1)). Found: C, 41.14; H, 2.60; W, 45.02.  $\text{C}_{14}\text{H}_{10}\text{WO}_3$  calc: C, 41.03; H, 2.46; W, 44.85%.

7. *Spirocyclopropane-9,9-fluorene and  $\text{Py}_3\text{Mo}(\text{CO})_3$* . The reaction was performed as described in exp. 2. 0.5 g (2.6 mmol) of spirocyclopropane-9,9-fluorene, 0.84 g (2.0 mmol) of  $\text{Py}_3\text{Mo}(\text{CO})_3$  and 1 ml (7 mmol) of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  in 50 ml of ether yielded, after three re-crystallizations from benzene with heptane, 0.2 g (27%) of lustrous yellow-green crystals of XVII, m.p. 139–140 °C.  $\nu(\text{CO})$ (ether) 1890, 1965  $\text{cm}^{-1}$ .

$^1\text{H NMR}$ : 0.8–1.06 (m, 4H, cyclopropane ring), 4.64 (1H, H(1)), 4.76 (m, 2H, H(2) + H(3)), 5.68 (1H, H(4)), 6.4 (1H, H(8)), 7.2 (m, 3H, H(5) + H(6) + H(8)). Found: C, 56.87, H, 3.65; Mo, 27.49.  $\text{C}_{18}\text{H}_{12}\text{MoO}_4$  calc: C, 58.06; H, 3.23; Mo, 25.8%.

8. *Spirocyclopropane-9,9-fluorene and  $\text{Py}_3\text{W}(\text{CO})_3$* . To a stirred mixture of 1.33 g (6.93 mmol) of spirocyclopropane-9,9-fluorene and 3.5 g (6.93 mmol) of  $\text{Py}_3\text{W}(\text{CO})_3$  in 60 ml of dibutyl ether was added, at 79–80 °C, 5 ml (31.2 mmol) of  $\text{Et}_2\text{O} \cdot \text{BF}_3$  in 10 ml of dibutyl ether. After 0.5 h the mixture was cooled and filtered through a 10 cm layer of  $\text{SiO}_2$  cooled with dry  $\text{CO}_2$ . After elution with ether and removal of the solvent in vacuo, the dry residue was extracted with pentane to give a solution of  $\sigma, \pi$ -chelated complex XIX,  $\nu(\text{CO})$ (ether) 1896, 1919 and 2014  $\text{cm}^{-1}$ . Attempts to isolate the pure complex sample failed.

Further extraction of the residue with benzene followed by purification on a  $\text{SiO}_2$  column at +4 °C and re-precipitation with heptane from benzene gave 0.25 g (7.5%) of  $\eta^6$ -complex XVIII, m.p. 178–180 °C (decomp.),  $\nu(\text{CO})$  ( $\text{CHCl}_3$ ) 1895, 1967  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ): 1.4 (m, 4H, cyclopropane ring), 4.46–4.70 (m, 3H, H(1) + H(2) + H(3)), 5.52–5.61 (m, 1H, H(4)), 6.45 (m, 1H, H(8)), 7.05–7.22 (m, 3H,



H(5) + H(6) + H(7)). Found: C, 47.96; H, 2.28; W, 40.04.  $C_{18}H_{12}O_3W$  calc: C, 46.98; H, 2.63; W, 39.96%.

9. *Reaction of spirocyclopropane-1,1-indene with  $(NH_3)_3Cr(CO)_3$ .* A stirred mixture of 0.2 g (1.45 mmol) of spirocyclopropane-1,1-indene and 0.19 g (1 mmol) of  $(NH_3)_3Cr(CO)_3$  in 30 ml of dioxane was heated at 100 °C during 7 h. The reaction mass was cooled to room temperature, filtered and evaporated to dryness. The residue was chromatographed on  $SiO_2$  plates eluting with benzene/petroleum ether system (1/1) the main yellow band with  $R_f = 0.3$  to 0.4 was collected and extracted with benzene. Precipitation from benzene with heptane gave 0.1 g (36%) of compound XI, m.p. 105 °C.

$\nu(CO)$  ( $CHCl_3$ ) 1890, 1971  $cm^{-1}$ .  $^1H$  NMR ( $C_6D_6$ ) 0.82–1.44 (m, 4H, cyclopropane ring), 4.46 (m, 3H, H(5) + H(6) + H(7)), 5.16 (m, 1H, H(4)), 5.66 (d, 1H, H(3),  $J(H(3),H(2))$  6 Hz), 6.14 (d, 1H, H(2),  $J(H(2),H(3))$  6 Hz). Found: C, 60.16; H, 4.37; Cr, 18.56.  $C_{14}H_{10}CrO_3$  calc: C, 60.22; H, 4.36; Cr, 18.62%.

#### 10. *Reaction of spirocyclopropane-9,9-fluorene with $(NH_3)_3Cr(CO)_3$*

This was carried out as described in exp. 9. Reaction of 0.5 g (2.6 mmol) of spirocyclopropane-9,9-fluorene with 0.56 g (3.0 mmol) of  $(NH_3)_3Cr(CO)_3$  with subsequent chromatography on a  $SiO_2$  column (3 × 30 cm) gave two complexes which were isolated pure. The first, eluted with the petroleum ether/benzene mixture, was the mononuclear  $\eta^6$ -complex XV, yield 0.4 g (47%), m.p. 176–177 °C.  $\nu(CO)$  (heptane) 1910, 1965  $cm^{-1}$ .  $^1H$  NMR ( $C_6D_6$ ) 0.9–1.56 (m, 4H, cyclopropane ring), 4.46 (m, 1H, H(1)), 4.56 (m, 2H, H(2) + H(3)), 5.44 (m, 1H, H(4)), 6.5 (m, 1H, H(8)), 7.18 (m, 3H, H(5) + H(6) + H(7)). Found: C, 65.63; H, 3.67; Cr, 16.05.  $C_{18}H_{12}CrO_3$  calc: C, 65.85; H, 3.66; Cr, 15.85%.

The second complex, eluted with benzene, was the binuclear complex XVI, m.p. 205–206 °C,  $\nu(CO)$  (heptane) 1900, 1960  $cm^{-1}$ .  $^1H$  NMR: 1.18 (s, 4H, cyclopropane ring), 4.08 (d, 2H, H(1) + H(8),  $J(H(1),H(2)) = J(H(7),H(8)) = 6$  Hz), 5.0 (d, 2H, H(5) + H(4),  $J(H(4),H(3)) = J(H(5),H(6)) = 6$  Hz), 4.38 (t, 4H, H(2) + H(3) and H(7) + H(8),  $J$  6 Hz).

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