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Heterometallic n,π-complexes of transition metals based on mesitylacetonitrile

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Abstract

A wide variety of neutral and cationic heterometallic n,π-complexes of transition metals $(MesCH_2CNM'L_k')ML_n$ (Mes = mesityl; $ML_n = Cr(CO)_3$, $Mo(CO)_3$, $Co_4(CO)_9$; $M'L'_k = W(CO)_5$, $Mn_2(CO)_9$, $Fe(CO)_2Cp$ (in the latter case a cationic complex is formed)) has been synthesised. The photochemical behaviour of the resulting compounds has been studied.

Introduction

We have previously produced a large number of neutral and cationic binuclear heterometallic π-complexes of transition metals based on dimesitylalkanes [1,2] and have studied their photochemical behaviour. These complexes relate to the π,π-type, as both metal-containing groups are linked with the ligand by π-bonds. It was of interest to study the possibility of synthesis of various binuclear n,π-type complexes, in which one of the metals is linked with the ligand by a π-bond, and the other one by a n-bond. Such compounds were thought of potential use for obtaining metallacycles. Mesitylacetononitrile was used as a model ligand.

Results and discussion

In the course of the investigation we found that a great variety of neutral and cationic binuclear n,π-complexes can be obtained by using various combinations of transition metals. In some cases (complexes **3**, **4**, **6**, **7**, **11**) π-arene coordination can be effected only after protection of nitrile by formation of n-complexes containing $W(CO)_5$, $Mn_2(CO)_9$ or $Fe(CO)_2Cp$ groups. The intermediate mononuclear n- and π-complexes (**2**, **5**, **9**, **10**, **12**) have also been obtained for the first time (Scheme 1).

Most of the resulting complexes are quite stable at room temperature. The yields and constants are presented in Table 1. Complexes **3**, **6**, **8** and **11** could not be obtained in analytically pure form and they are identified by IR spectra in the metal-carbonyl region (Table 2).

It is interesting that the interaction of complex **12** with $Mn_2(CO)_{10}$ under

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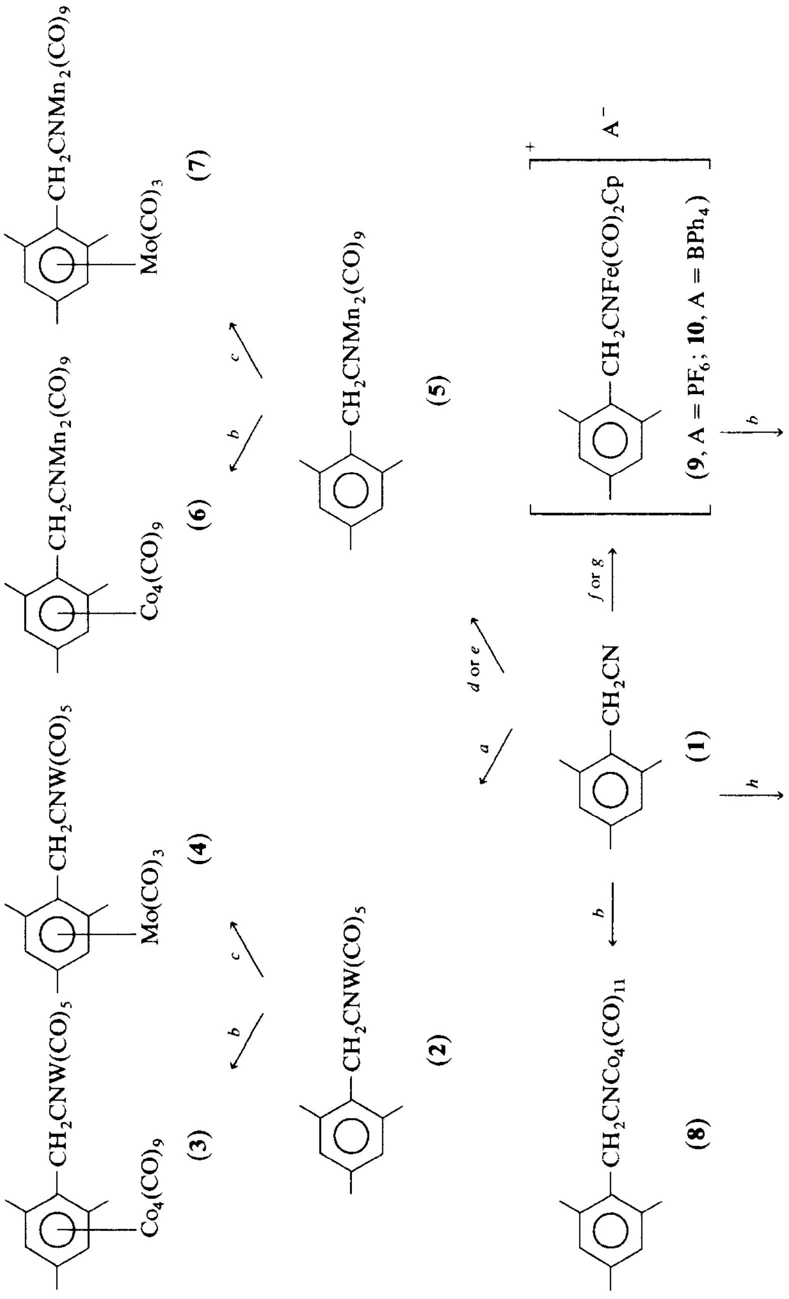
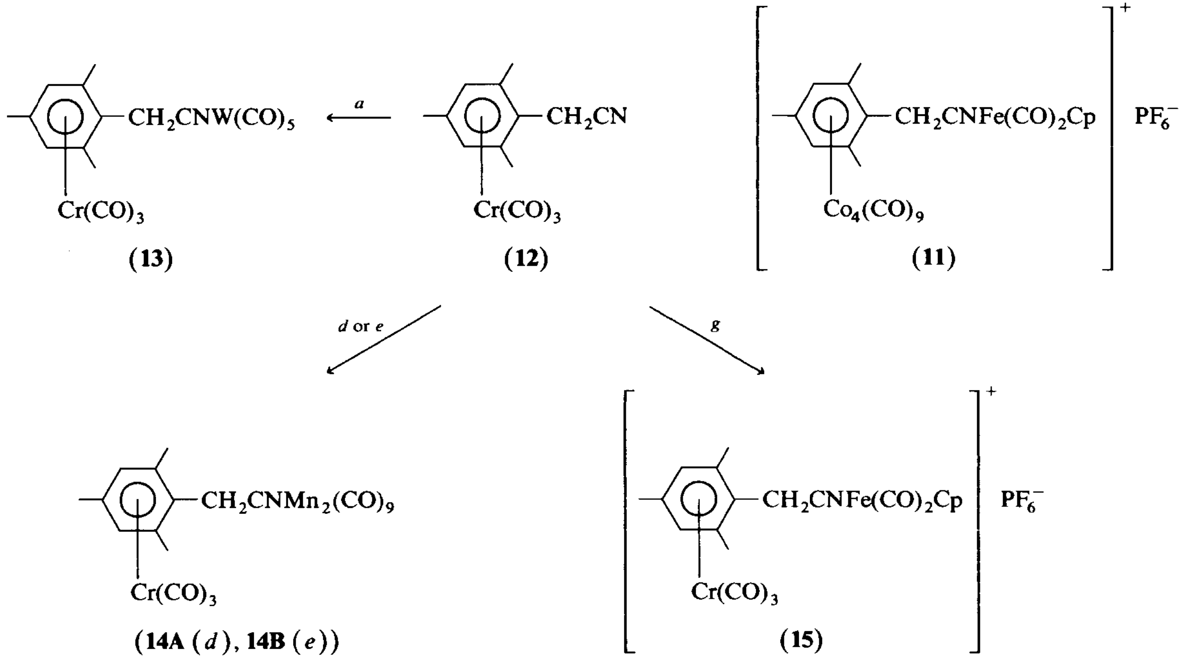

CH2CNW(CO)5
Co4(CO)9
(3)
CH2CNW(CO)5
Mo(CO)3
(4)
CH2CNMn2(CO)9
Co4(CO)9
(6)
CH2CNMn2(CO)9
Mo(CO)3
(7)
b
c
CH2CNW(CO)5
(2)
b
c
CH2CNMn2(CO)9
(5)
a
d or e
CH2CNCo4(CO)11
(8)
b
CH2CN
(1)
h
f or g
CH2CNFe(CO)2Cp
+
A⁻
(9, A = PF6; 10, A = BPh4)
b



Scheme 1. (*a*) W(CO)$_6$, benzene, *hν* [3,4]; (b) Co$_2$(CO)$_8$, hexane, Δ [1]; (*c*) Py$_3$Mo(CO)$_3$, BF$_3$·OEt$_2$, ether [3,5]; (*d*) Mn$_2$(CO)$_{10}$, benzene, *hν* [6]; (*e*) Mn$_2$(CO)$_{10}$, Me$_3$NO [7]; (*f*) [Fe(CO)$_2$(H$_2$O)Cp]BPh$_4$ [8]; (*g*) [Fe(CO)$_2$Cp]$_2$, Fe$_2$(SO$_4$)$_3$, MeOH/NH$_4$PF$_6$ or NaBPh$_4$; (*h*) Cr(CO)$_6$, diglyme+heptane, Δ [3].

Table 1

Experimental data

Compound	Yield (%)	m.p. (with dec.) (°C)	Anal. Found (calc.) (%)			Empirical formula
			C	H	N	
$MesCH_2CNW(CO)_5$	40	100–102	39.90	2.96	2.92	$C_{16}H_{13}NO_5W$
(2)			(39.77)	(2.71)	(2.90)	
$(CO)_3MoMesCH_2CNW(CO)_5$	12	48–52 [a]	34.42	1.80	2.00	$C_{19}H_{13}MoNO_8W$
(4)			(34.41)	(1.98)	(2.11)	
$MesCH_2CNMn_2(CO)_9$	75	130–132	45.96	2.90	3.33	$C_{20}H_{13}Mn_2NO_9$
(5)	(45)		(46.09)	(2.51)	(2.69)	
$(CO)_3MoMesCH_2CNMn_2(CO)_9$	32	98–108 [a]	40.06	1.86	2.25	$C_{23}H_{13}Mn_2MoNO_{12}$
(7)			(39.40)	(1.87)	(2.00)	
$[MesCH_2CNFe(CO)_2Cp]PF_6$	30	153–156 [a]	44.83	3.54	2.76	$C_{18}H_{18}F_6FeNO_2P$
(9)			(44.93)	(3.77)	(2.91)	
$[MesCH_2CNFe(CO)_2Cp]BPh_4$	60	134–139	76.56	5.47	2.25	$C_{42}H_{38}BFeNO_2$
(10)			(76.96)	(5.84)	(2.14)	
$(CO)_3CrMesCH_2CN$	65	140–141	56.78	4.10	5.00	$C_{14}H_{13}CrNO_3$
(12)			(56.95)	(4.44)	(4.74)	
$(CO)_3CrMesCH_2CNW(CO)_5$	36	152–154	36.98	2.23	2.08	$C_{19}H_{13}CrNO_8W$
(13)			(36.86)	(2.12)	(2.26)	
$(CO)_3CrMesCH_2CNMn_2(CO)_9$- eq	20	129–133	42.41	2.09	2.34	$C_{23}H_{13}CrMn_2NO_{12}$
(14A)			(42.03)	(1.99)	(2.13)	
$(CO)_3CrMesCH_2CNMn_2(CO)_9$- ax	64	120–122	42.23	2.02	1.95	$C_{23}H_{13}CrMn_2NO_{12}$
(14B)			(42.03)	(1.99)	(2.13)	
$[(CO)_3CrMesCH_2CNFe(CO)_2Cp]PF_6$	21	58–68	41.04	3.00	1.99	$C_{21}H_{18}CrF_6NO_2P$
(15)			(40.86)	(2.94)	(2.27)	

[a] Decomposes without melting.

different conditions seems to produce different isomers of product **14**. Both of these isomers correspond to the suggested formula with respect to elemental analysis, but have different R_f on silufol and IR spectra. UV irradiation by the method in ref. 6 produces derivative **14A** having an equatorial arrangement of the substituent in manganese carbonyl, as determined by the IR spectrum, as always takes place for nitrile ligands [6,7]. At the same time the reaction in the presence of Me_3NO by the method [7] seems to form the axial isomer **14B** preferentially, which was earlier observed only for phosphines [6,7]. The reduced number of $\nu(C{\equiv}O)$ bands in the IR spectrum of this compound in CH_2Cl_2 (Table 2) supports this assumption. It is possible that the reason for such an unusual result is the large size of the incoming substituent, since interaction of $Mn_2(CO)_{10}$ with the original ligand **1**, both photochemically and in the presence of Me_3NO forms only the complex **5** with equatorial arrangement of a nitrile ligand (all these conclusions are derived from the analysis of IR spectra, see Table 2). It is interesting that UV irradiation of a benzene solution leads to a partial conversion of the complex **14B** into **14A** (this process is accompanied by significant decomposition).

The NMR spectra of the investigated compounds (Table 3) demonstrate that the formation of the π-complex (compound **12**), is, as usual, accompanied by a significant shift of the signal of aromatic protons to the strong field (by 1.6 ppm),

Table 2

IR spectral data

Compound	ν(C≡N) (KBr pellet)	ν(C≡O)	
		heptane	CH_2Cl_2
$MesCH_2CN$ **(1)**	2250m	–	–
$MesCH_2CNW(CO)_5$ **(2)**	–	2073w, 1940s, 1922m	2072w, 1934s, 1894m
$(CO)_9Co_4MesCH_2CNW(CO)_5$ **(3)**	–	2072w, 2040s, 2033s, 2010w, 1939s, 1921m, 1852w, 1840w	–
$(CO)_3MoMesCH_2CNW(CO)_5$ **(4)**	–	–	2072w, 1965s, 1936s, 1888s
$MesCH_2CNMn_2(CO)_9$ **(5)**	2285vw	2087w, 2021s, 2001m, 1988s, sh, 1983s, 1962m, 1943w	2087w, 2020s, 1989s, 1978s, 1958m sh, 1928m
$(CO)_9Co_4MesCH_2CNMn_2(CO)_9$ **(6)**	–	2071m, 2040w, 2029s, 2010m, 1998w, 1992w, 1897w, 1825w, 1808w	–
$(CO)_3MoMesCH_2CNMn_2(CO)_9$ **(7)**	2286vw	–	2088w, 2020s, 1988s, 1977s, 1963s, 1935m, 1887m
$MesCH_2CNCo_4(CO)_{11}$ **(8)**	–	2082w, 2060m, 2051m, 2043s, 2034s, 2012w, 1854m, 1841m	– –
$[MesCH_2CNFe(CO)_2Cp]PF_6$ **(9)**	–	–	2075, 2031
$[MesCH_2CNFe(CO)_2Cp]BPh_4$ **(10)**	–	–	2077, 2036
$[(CO)_9Co_4MesCH_2CNFe(CO)_2Cp]PF_6$ **(11)**	–	–	2074s, 2060s, 2049s, 2031s, 1851m, 1816w
$(CO)_3CrMesCH_2CN$ **(12)**	2267m	1971, 1908, 1899	1960, 1884
$(CO)_3CrMesCH_2CNW(CO)_5$ **(13)**	–	–	2074w, 1964s, 1936s, 1893s
$(CO)_3CrMesCH_2CNMn_2(CO)_9$- eq **(14A)**	2285vw	2083vw, 2021s, 2003m, 1985s, 1972s, 1958m, 1940w, 1910m, 1896w	2088vw, 2020s, 1990s, 1977s, 1964m sh, 1931s, 1886w
$(CO)_3CrMesCH_2CNMn_2(CO)_9$- ax **(14B)**	2285vw	2087vw, 2021s, 2003m, 1985s, 1971s, 1958m, 1945w, 1911m, 1899w	2087w, 2020s, 1979s, 1960s, 1886m
$[(CO)_3CrMesCH_2CNFe(CO)_2Cp]PF_6$ **(15)**	–	–	2076, 2035, 1958, 1883
16	–	–	2071w, 1971m, 1930s, 1892m, 1768w
17	–	–	2075w, 1965m, 1937s, 1888m, 1768w
$(CO)_2(PPh_3)CrMesCH_2CNW(CO)_5$ **(18)**	–	–	2015w, 1962s, 1924w sh, 1878v s, 1820m
$(CO)_2(PPh_3)CrMesCH_2CNMn_2(CO)_9$ **(20)**	–	1969s, 1906m, 1897m, 1842w	1960, 1872s, 1816m

Table 3

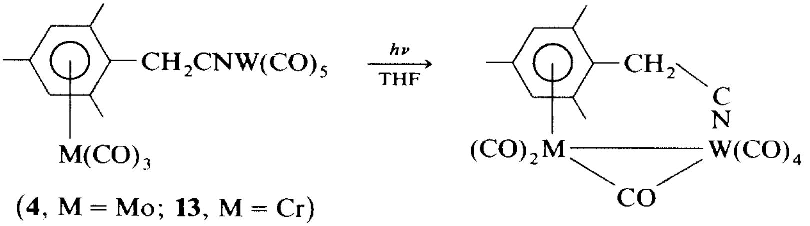
^{1}H NMR spectral data (δ, ppm) [a]

Compound [b]	arom.	CH_2	Me(o)	Me(p)	Cp
L (**1**)	6.88	3.73	2.31	2.20	–
$LW(CO)_5$ (**2**)	6.93	4.27	2.36	2.23	–
$LMn_2(CO)_9$ (**5**)	6.89	4.20	2.33	2.21	–
$[LFe(CO)_2Cp]PF_6$ (**9**)	6.91	4.20	2.29	2.23	5.63
$LCr(CO)_3$ (**12**)	5.31	3.80	2.39	2.18	–
$LCr(CO)_3W(CO)_5$ (**13**)	5.30	4.32	2.42	2.19	–
$LCr(CO)_3Mn_2(CO)_9$-eq (**14A**)	5.30	4.28	2.37	2.18	–
$LCr(CO)_3Mn_2(CO)_9$-ax (**14B**)	5.31	4.30	2.37	2.18	–

[a] Signals are singlets. [b] L = $Me_3C_6H_2CH_2CN$.

whereas the position of the signal of protons of the CH_2-group does not change. On the contrary, when the n-complex is formed (compounds **2**, **5**, **9**), the position of aromatic protons does not change, whereas the signal of the CH_2-group is shifted to the weak field by 0.5 ppm. A change in the position of aromatic and CH_2 protons occurs simultaneously in binuclear n,π-complexes **13** and **14** by using the additivity principle, the spectra of complexes **14A** and **14B**, as expected, being almost the same.

We have studied further the photochemical behaviour of some of the resulting n,π-complexes. Compounds **4** and **13** were found to form unstable metallacycles **16** and **17** by UV irradiation. These derivatives are characterized by IR spectra in the metal-carbonyl region, which in addition to the terminal, contain also bands of bridging CO groups (Table 2).

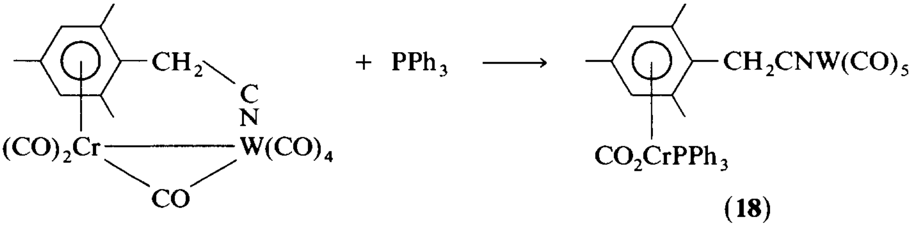


(**4**, M = Mo; **13**, M = Cr)

(**16**, M = Mo; **17**, M = Cr)

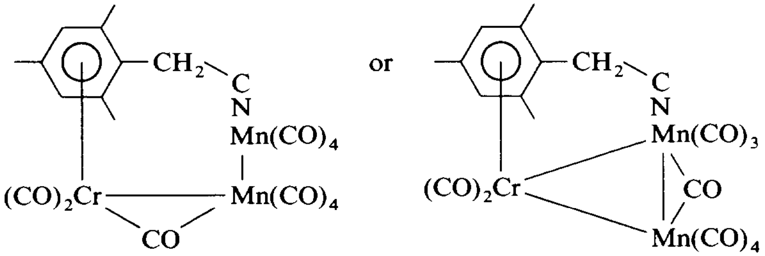
It should be noted that we have earlier made an attempt to synthese analogous compounds based on ω-arylpropyo- and -butyronitriles [3,4], but the greater number of methylene groups in the bridge did not bring about any substantial increase in the stability of the resulting metallacycles.

When triphenylphosphine is added, complex **17** is rapidly converted into a yellow-orange product which was assumed to have the structure **18** in accordance with the IR spectrum.



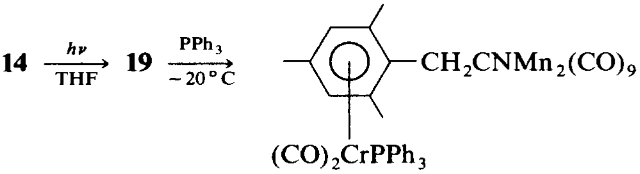
(17) **(18)**

When complexes **14A,B** are subjected to UV irradiation, the reaction mixture always contains a significant amount of the starting compound. The irradiation products are quite unstable and are readily degraded when an attempt is made to recover them in pure form. The appearance of new bands in the IR spectrum at 2042m, 2006s and 1824w cm^{-1} indicates the formation of new products. The presence of the last band makes it possible to assume the formation of compound **19** have a bridging CO group:



(19)

This assumption is also advantageous in that the reaction of compound **19** with PPh$_3$ gives a product, although in very low yield, to which the structure **20** can be ascribed according to IR spectrum:



(20)

When a solution of **15** in THF is UV-irradiated, after just only three hours only complex **9** is observed, i.e. in this case the Cr(CO)$_3$-group is readily eliminated.

Experimental

All operations for the synthesis and isolation of the investigated compounds were carried out in an argon atmosphere using absolute solvents. IR spectra were recorded on a Specord 75 IR (in solutions) and UR-20 (in KBr pellets) spectrophotometers. NMR spectra were measured on a Bruker WP-200 SY spectrometer in CD_3COCD_3 with HMDS as an internal standard. A DRT-220 lamp was used for UV irradiation. Most compounds were obtained by standard procedures (see Scheme 1).

Preparation of $MesCH_2CNMn_2(CO)_9$ *(5)*

(1) A solution of $MesCH_2CN$ (0.4 g, 2.5 mmol) and $Mn_2(CO)_{10}$ (1 g, 2.5 mmol) in 200 ml of benzene was irradiated with UV light for 7 h. The solvent was removed *in vacuo* and the residue was chromatographed on a Al_2O_3 column. The first light-yellow band containing $Mn_2(CO)_{10}$ was eluted with a 1 : 5 benzene/petroleum ether mixture. The second bright-yellow band containing 0.6 g (45%) of product **5** was eluted with a 1 : 1 mixture. The product was reprecipitated with heptane from CH_2Cl_2.

(2) To a stirred solution of $MesCH_2CN$ (0.4 g, 2.5 mmol) and $Mn_2(CO)_{10}$ (1 g, 2.5 mmol) in 50 ml of CH_2Cl_2 was added a solution of $Me_3NO \cdot 2H_2O$ (0.3 g, 2.7 mmol) in 20 ml of CH_2Cl_2 and the stirring continued for 3 h. The solvent was removed *in vacuo*. Chromatography on an Al_2O_3 column gave 1 g (75%) of product **5**, identified by IR spectrum and R_f on silufol.

Preparation of $[MesCH_2CNFe(CO)_2Cp]PF_6$ *(9)*

A mixture of $MesCH_2CN$ (0.5 g, 3.15 mmol), $[Fe(CO)_2Cp]_2$ (0.5 g, 1.4 mmol) and $Fe_2(SO_4)_3 \cdot 9H_2O$ (1 g, 1.8 mmol) was magnetically stirred in 50 ml of methanol for 15 h. The solvent was removed *in vacuo*. The product was extracted with water, filtered and precipitated with an excess of a saturated aqueous NH_4PF_6 solution. The precipitate was filtered off, washed with a small amount of water, dried and reprecipitated from CH_2Cl_2 with ether to give a light-yellow complex **9**.

Compound **10** was obtained either analogously or (in lower yield) by reacting $MesCH_2CN$ with $[Fe(CO)_2(H_2O)Cp]BPh_4$ [8].

Preparation of $[(CO)_9Co_4MesCH_2CNFe(CO)_2Cp]PF_6$ *(11)*

A mixture of complex **9** (0.1 g, 0.2 mmol) and $Co_2(CO)_8$ (0.34 g, 1 mmol) was refluxed in hexane (60 ml) for 8 h. The solvent was decanted, the residue washed with pentane and reprecipitated with heptane from CH_2Cl_2 to give 20 mg (14%) of the product corresponding to formula **11** in accordance with the IR spectrum.

Preparation of $(CO)_3CrMesCH_2CNMn_2(CO)_9$ *(14)*

(1) A solution of **12** (0.3 g, 1 mmol) and $Mn_2(CO)_{10}$ (0.5 g, 1.25 mmol) in 100 ml of benzene was irradiated with UV light at 10–20 °C with stirring using a magnetic bar for 22 h. The solvent was removed in vacuo and the residue was chromatographed on an Al_2O_3 column. In addition to a small amount of $Mn_2(CO)_{10}$ (the first band) and 85 mg (28%) of the starting compound **12** (the third band), 0.13 g (20%) of complex **14A** was obtained (the second band). A light-yellow product was reprecipitated with heptane from CH_2Cl_2.

(2) To a stirred solution of **12** (0.2 g, 0.68 mmol) and $Mn_2(CO)_{10}$ (0.5 g, 1.25 mmol) in 50 ml of CH_2Cl_2 was added a solution of $Me_3NO \cdot 2H_2O$ (0.15 g, 1.35 mmol) in 20 ml of CH_2Cl_2 and the mixture was further stirred for 3 h. The solvent was removed in vacuo and the residue was chromatographed on an Al_2O_3 column. In addition to $Mn_2(CO)_{10}$ (the first band) and 26 mg (6%) of **14A** (the second

band), 0.28 g (64%) of product **14B** was obtained (the third band). A yellow compound was reprecipitated with heptane from CH_2Cl_2.

Preparation of [(CO)$_3$CrMesCH$_2$CNFe(CO)$_2$Cp]PF$_6$ (15)

A mixture of compound **12** (0.2 g, 0.68 mmol), $[Fe(CO)_2Cp]_2$ (0.2 g, 0.56 mmol) and $Fe_2(SO_4)_3 \cdot 9H_2O$ (0.4 g, 0.72 mmol) was magnetically stirred in 50 ml of methanol for 16 h. The solvent was removed *in vacuo*. The product was extracted with water, filtered and precipitated with an excess of a saturated aqueous NH_4PF_6 solution. The precipitate was filtered off, washed with a small amount of water, dried and reprecipitated from CH_2Cl_2 with ether to give a light-yellow complex **15**.

Irradiation of complex 4

A solution of **4** (0.2 g, 0.3 mmol) in 100 ml of THF was irradiated with UV light at 10–20 °C for 2 h. The solution turned from yellow to very dark red. The solvent was removed in vacuo and the rapidly degradable oily complex **16** was identified by the IR spectrum.

Irradiation of complex 13

As in the previous experiment, the unstable derivative **17** is formed from irradiation of **13**.

If at the conclusion of irradiation of a solution (0.2 g, 0.33 mmol) of complex **13** in 100 ml THF, one adds 0.26 g (1 mmol) of PPh_3 and continues stirring at room temperature, 1 hour later the solution becomes light-orange. The solvent was removed in vacuo and the residue was chromatographed on an Al_2O_3 column. From the first, yellow band, eluted with a benzene/petroleum ether mixture (2/1), 0.076 g (38%) of the initial **13** was recovered; from the second, dark-yellow band, eluted with benzene, 0.04 g (15%) of yellow-orange product **18** was obtained which could not be isolated in analytically pure form and was identified by the IR spectrum.

Irradiation of complexes 14

(a) A solution of **14A** (0.1 g, 0.15 mmol) in 100 ml of THF was irradiated with UV light for 7 h. After the solvent was removed *in vacuo* (significant decomposition was observed), the IR spectrum in CH_2Cl_2 was measured. Besides the bands of the starting **14A** there were also 2042m, 2006s and 1824w (cm^{-1}) bands. When an attempt was made to separate the product from the starting compound by chromatography, it decomposed. If after irradiation 0.1 g (0.4 mmol) of PPh_3 was added and stirring was continued, 1 hour later the solution turned from dark-red to light-orange. The solvent was removed *in vacuo*, and the residue chromatographed on a SiO_2 column. In addition to a light-yellow band eluted with a benzene/petroleum ether mixture (1/1) and containing predominantly triphenylphosphine, a dark-yellow band containing 12 mg of compound **20** was eluted with pure CH_2Cl_2.

(b) Analogously with the previous experiment irradiation of **14B** gave a product which contained in the IR spectrum, in addition to the bands of the starting compound, bands 2042m, 2006s and 1824w (cm^{-1}). After the reaction with PPh_3, similar to that described above, 9 mg of product **20** was isolated by silica gel column chromatography.

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