Organometallic Nitrosyl Chemistry. Part 3.[1] Some Aspects of the Chemistry of Bis[(η-cyclopentadienyl)dinitrosylchromium]

By **Brian W. S. Kolthammer** and **Peter Legzdins,*** Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1W5

The compound [{Cr(cp)(NO)$_2$}$_2$] (cp = η-cyclopentadienyl), like its isoelectronic carbonyl analogue [{Fe(cp)(CO)$_2$}$_2$], is cleaved by I_2, HCl(aq), and NOCl at room temperature to give [Cr(cp)(NO)$_2$X] (X = I or Cl). However, unlike its carbonyl analogue, the chromium dimer abstracts all the chlorine ligands from $SnCl_4$, MCl_2 (M = Hg, Sn, or Pb), [Fe(cp)(CO)$_2$Cl], and [Mn(CO)$_5$Cl] in refluxing polar organic solvents to form [Cr(cp)(NO)$_2$Cl]. The other products in these reactions are the metals (M), [{Fe(cp)(CO)$_2$}$_2$], and [Mn$_2$(CO)$_{10}$] respectively. Under certain conditions (such as heating in refluxing toluene) the chromium dimer is converted into [(ON)(cp)Cr(μ-NO)(μ-NH$_2$)Cr(cp)(NO)], whereas the related manganese dimer [{Mn(C$_5$H$_4$Me)(CO)(NO)}$_2$] is transformed into [Mn(C$_5$H$_4$Me)(CO)$_3$] and [Mn$_3$(C$_5$H$_4$Me)$_3$(NO)$_4$] in refluxing thf. Both these latter conversions occur in low yields.

THE compound bis[(η-cyclopentadienyl)dinitrosylchromium], [{Cr(cp)(NO)$_2$}$_2$] (cp = η-C_5H_5), was first obtained[2] in 1964 by the sodium tetrahydroborate reduction of [Cr(cp)(NO)$_2$Cl] in an aqueous medium. Unfortunately, only relatively small quantities of the red-violet compound were available due to the 5% yield of the original preparation, and an extensive study of its characteristic reactions could not be made. We have recently discovered that [{Cr(cp)(NO)$_2$}$_2$] can be very conveniently synthesized in higher yields (56—75%) by reducing [Cr(cp)(NO)$_2$Cl] with either zinc amalgam in tetrahydrofuran (thf)[1] or sodium amalgam in benzene.[3] In this manner we have obtained sufficient of the dimer to enable us to investigate its physical and chemical properties more fully than was previously possible. We

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[1] Part 2, J. K. Hoyano, P. Legzdins, and J. T. Malito, *J.C.S. Dalton*, 1975, 1022.

[2] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 791.

[3] B. W. S. Kolthammer, P. Legzdins, and J. T. Malito, *Inorg. Synth.*, **19**, in the press.

report the results of these investigations and contrast the chemistry of $[\{Cr(cp)(NO)_2\}_2]$ with that exhibited by its isoelectronic carbonyl analogue, $[\{Fe(cp)(CO)_2\}_2]$.

EXPERIMENTAL

All the chemicals used were of reagent grade or comparable purity. The reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was ascertained by elemental analyses and/or m.p. determinations. Melting points were determined in capillaries and are uncorrected. All the solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use, and all the manipulations were made in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the band of polystyrene film at 1 601 cm^{-1}. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates T60 spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded at 70 eV * on Atlas CH4B or A.E.I. MS50 spectrometers, using the direct-probe-insertion method with the assistance of Dr. G. Eigendorf and Mr. G. Gunn. Elemental analyses were by Mr. P. Borda of this department.

TABLE 1

Reactions of $[\{Cr(cp)(NO)_2\}_2]$ with some halogen-containing compounds

Reactant (amount) [a]	Dimer (amount) [a]	Solvent (volume/cm^3)	Reaction conditions	Products (yield/%)	Method of isolation
NOCl [b] (in CH_2Cl_2) [c]	0.08, 0.23	CH_2Cl_2 (35)	Immediate at 25 °C	$[Cr(cp)(NO)_2Cl]$ [c] (>95)	removal of solvent *in vacuo*
$SnCl_4$ (0.23, 0.90)	0.52, 1.5	thf (50)	Reflux, 17 h	$[Cr(cp)(NO)_2Cl]$ (69)	chromatography on Florisil with CH_2Cl_2 as eluant
$HgCl_2$ (0.27, 1.0)	0.35, 1.0	thf (60)	Reflux, 24 h	$[Cr(cp)(NO)_2Cl]$ (>95) + Hg(l)	chromatography on Florisil
$SnCl_2$ (0.19, 1.0)	0.35, 1.0	thf (60)	Reflux, 24 h	$[Cr(cp)(NO)_2Cl]$ (>95)	chromatography on Florisil
$PbCl_2$ (0.28, 1.0)	0.35, 1.0	thf (60) or Bu^nOH (60)	Reflux, 24 h or Reflux, 6 h	$[Cr(cp)(NO)_2Cl]$ (>95)	chromatography on Florisil

[a] Given in g and in mmol. [b] G. Pass and H. Sutcliffe, 'Practical Inorganic Chemistry,' Chapman and Hall, London, 1968, pp. 145—146. [c] Ref. 4.

Reactions of $[\{Cr(cp)(NO)_2\}_2]$.—*With* HCl(aq). To a stirred solution of $[\{Cr(cp)(NO)_2\}_2]$ (0.17 g, 0.50 mmol) in ethanol (25 cm^3) and dichloromethane (5 cm^3) was added 12 mol dm^{-3} HCl (1 cm^3, 12 mmol) at room temperature. The reaction mixture retained its original red-violet colour until air was bubbled through it for *ca.* 10 min, whereupon it became green-brown. At the end of this time the final mixture was taken to dryness *in vacuo* and the residue was extracted with dichloromethane (30 cm^3). The extract was filtered and an i.r. spectrum of the filtrate showed it to contain $[Cr(cp)(NO)_2Cl]$.[4] The organometallic product (0.11 g, 52%) was obtained by removing the solvent from the filtrate *in vacuo*.

With I_2. To a stirred dichloromethane solution (40 cm^3) of $[\{Cr(cp)(NO)_2\}_2]$ (0.35 g, 1.0 mmol) at room temperature was added I_2 (0.30 g, 1.0 mmol). The reaction mixture immediately changed colour from red-violet to yellow-brown. It was stirred for 1 h, at which time an i.r. spectrum revealed $[Cr(cp)(NO)_2I]$ [2] as the only organometallic product. The product could be isolated virtually quantitatively by taking the final solution to dryness *in vacuo*.

The reactions of $[\{Cr(cp)(NO)_2\}_2]$ with other inorganic halogen-containing compounds were performed similarly, and they are summarized in Table 1.

With $[Fe(cp)(CO)_2Cl]$. A mixture of $[\{Cr(cp)(NO)_2\}_2]$ (0.18 g, 0.50 mmol) and $[Fe(cp)(CO)_2Cl]$ [5] (0.21 g, 1.0 mmol) in thf (40 cm^3) was heated under reflux for 4.5 h, during which time the reaction mixture developed a yellowish tinge to its violet colouration. An i.r. spectrum of the final reaction mixture at room temperature indicated that it contained some of the original reactant $[\{Cr(cp)(NO)_2\}_2]$ as well as the products $[Cr(cp)(NO)_2Cl]$ and $[\{Fe(cp)(CO)_2\}_2]$.[6] In order to confirm the presence of the last compound, the final mixture was chromatographed on alumina (activity grade V) with thf as eluant. The first red-violet band to separate was collected and the solvent was removed from the eluate *in vacuo*. The residue was identified as $[\{Fe(cp)(CO)_2\}_2]$ by comparison of its i.r. (in thf) and n.m.r. (in C_6D_6) spectra with spectra of an authentic sample of the compound.

With $[Mn(CO)_5Cl]$. To a solution of $[\{Cr(cp)(NO)_2\}_2]$ (0.11 g, 0.31 mmol) in thf (40 cm^3) was added $[Mn(CO)_5Cl]$ [6] (0.14 g, 0.61 mmol). The resulting red-violet solution was stirred at reflux for 30 h whereupon it became brown. Comparative i.r. spectroscopy of the final reaction mixture at room temperature revealed it to contain $[Mn(CO)_5Cl]$ and $[Mn_2(CO)_{10}]$ as the only carbonyl compounds, and $[Cr(cp)(NO)_2Cl]$ and $[\{Cr(cp)(NO)_2\}_2]$ as the only nitrosyl compounds in approximately equal amounts. No attempt was made to isolate the various compounds.

With $SnPh_3Cl$. To a solution of $[\{Cr(cp)(NO)_2\}_2]$ (0.50 g, 1.4 mmol) in thf (80 cm^3) was added $SnPh_3Cl$ (1.1 g, 2.8 mmol). The resulting solution was stirred at reflux until the nitrosyl i.r. absorptions due to the initial reactant had disappeared (8 d) and the colour of the solution changed from red-violet to brown. The final reaction mixture was taken to dryness *in vacuo* at ambient temperature. The residue was dissolved in a minimum amount of benzene and was chromatographed on a Florisil column (2 × 20 cm). Elution of the column with benzene produced three bands: (*i*) a narrow red-violet band that moved quickly down the column; (*ii*) a light green band that carried directly behind the first band; and (*iii*) a broad green-gold band that was well resolved from the first two bands. All the three fractions were collected and concentrated *in vacuo*. Infrared spectra of the eluates revealed components (*i*) and (*iii*) to be $[\{Cr(cp)(NO)_2\}_2]$ and [Cr-

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* Throughout this paper: 1 eV = 1.60×10^{-19} J.

[4] P. Legzdins and J. T. Malito, *Inorg. Chem.*, 1975, **14**, 1875.

[5] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

[6] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

(cp)$(NO)_2Cl$] respectively. Eluate (*ii*) was ultimately taken to dryness *in vacuo* and the residue was recrystallized from dichloromethane–hexane as dark green crystals (*ca.* 0.1 g) of [$Cr_2(cp)_2(NO)_3(NH_2)$] (Found: C, 34.7; H, 3.60; N, 16.2. Calc. for $C_{10}H_{12}Cr_2N_4O_3$: C, 35.3; H, 3.55; N, 16.5%).

Pyrolyses.—Of [{Cr(cp)$(NO)_2$}$_2$]. A stirred red-violet solution of [{Cr(cp)$(NO)_2$}$_2$] (0.75 g, 2.1 mmol) in toluene (100 cm^3) was heated under gentle reflux for 24 h. During this time the solution darkened and a black solid precipitated. The solvent was removed from the final cooled reaction mixture *in vacuo*, and the residue was redissolved in dichloromethane. The dichloromethane solution was then syringed on to a Florisil column (2 × 10 cm) and a green band was eluted with this same solvent. Crystals (0.11 g, 15%) of [$Cr_2(cp)_2(NO)_3(NH_2)$] were obtained from the eluate as described in the preceding section. An intense brown band was next eluted from the Florisil column with thf as eluant, and the eluate was taken to dryness *in vacuo*. The residue was crystallized from dichloromethane–hexane as a red-brown microcrystalline solid (0.30 g) (Found: C, 45.2; H, 4.00; N, 10.8%) which displayed a parent peak in its mass spectrum at *m/e* 531.899.

Of [{Mn(C_5H_4Me)(CO)(NO)}$_2$]. A red-violet solution of [{Mn(C_5H_4Me)(CO)(NO)}$_2$] (0.97 g, 2.5 mmol; prepared in a manner identical to that reported[2] for [{Mn(cp)(CO)(NO)}$_2$]) in thf (50 cm^3) was heated under reflux with gentle stirring for 20 h. At the end of this time the reaction mixture had deposited some black-brown insoluble material and the supernatant liquid had a dark green tinge. An i.r. spectrum of the supernatant at room temperature did not exhibit the carbonyl and nitrosyl absorptions of the starting compound. The final reaction mixture was taken to dryness *in vacuo*. Dichloromethane (15 cm^3) was added to the residue, and the mixture (a green-black solution and a rust-coloured solid) was transferred to the top of a Florisil column (2 × 13 cm) for subsequent chromatography. Elution of the column with dichloromethane resulted in the development of two distinct bands. The first pale orange band, which carried quickly down the column, was collected, and comparative i.r. spectroscopy of this fraction indicated that it contained a very small amount of [Mn(C_5H_4Me)$(CO)_3$]. The second fraction to be eluted from the column was a very broad green-black band which required *ca.* 300 cm^3 of dichloromethane for complete elution. This eluate was concentrated *in vacuo* to a volume of 25 cm^3, and sufficient hexane was then added to induce the crystallization of [$Mn_3(C_5H_4Me)_3(NO)_4$] (0.09 g, 10%) (Found: C, 41.4; H, 4.00; N, 10.9. Calc. for $C_{18}H_{21}Mn_3N_4O_4$: C, 41.4; H, 4.05; N, 10.7%).

RESULTS AND DISCUSSION

The compound [{Cr(cp)$(NO)_2$}$_2$] bears a remarkable resemblance to its isoelectronic carbonyl analogue [{Fe(cp)$(CO)_2$}$_2$]. Both compounds are red-purple solids which are insoluble in water, sparingly soluble in non-polar organic solvents, and soluble in polar organic solvents to give solutions which oxidize gradually in air. In the solid state both dimers exhibit *trans* ligand-bridged molecular structures,[7] but the iron compound can also be isolated in a *cis* bridged form under certain conditions.[8] Both molecules also undergo rapid intramolecular rearrangement at room temperature,[9] existing in solution as an equilibrating mixture of isomeric structures.

The two compounds do exhibit striking differences in some of their physical properties. The 70-eV mass-spectral data of both dimers are shown in Table 2. In contrast to the reported spectrum of [{Fe(cp)$(CO)_2$}$_2$],[10] the high-resolution mass spectrum of the chromium dimer reveals the sequential loss of nitrosyl groups, but the most abundant species present is the dimeric [$Cr_2(cp)_2(NO)$]$^+$ ion. Indeed, ions containing two metal atoms are generally much more abundant for the chromium compound. Migration of the cyclopentadienyl group group between metal atoms occurs much less readily than for the iron compound as evidenced by the markedly less abundant [$Cr(cp)_2$]$^+$ ion. Fission of the chromium dimer also occurs in a symmetrical manner {*i.e.* no ions of the type [Cr(cp)$(NO)_3$]$^+$ are detectable}, but various ions {such as the relatively abundant [Cr_2(cp)O]$^+$ and [Cr_2O]$^+$} in the mass spectrum of the chromium compound have no counterparts in the fragmentation pattern of the iron compound. Similar oxo-ions have been previously observed in the mass spectra of other organometallic nitrosyl compounds.[11]

TABLE 2

High-resolution mass spectral data for [{Cr(cp)$(NO)_2$}$_2$]

m/e Found [a]	*m/e* Calc.	Relative abundance	Assignment [b]	Relative abundance (Fe) [c]
353.952	353.951	45.1	[$Cr_2(cp)_2(NO)_4$]$^+$	9
323.953	323.953	34.2	[$Cr_2(cp)_2(NO)_3$]$^+$	6
293.955	293.955	9.9	[$Cr_2(cp)_2(NO)_2$]$^+$	10
263.957	263.957	100.0	[$Cr_2(cp)_2(NO)$]$^+$	4
198.919	198.918	13.4	[Cr_2(cp)(NO)]$^+$	0
184.915	184.915	73.8	[Cr_2(cp)O]$^+$	0
182.018	182.019	9.5	[$Cr(cp)_2$]$^+$	70
176.976	176.976	14.0	[Cr(cp)$(NO)_2$]$^+$	19
146.978	146.978	12.0	[Cr(cp)(NO)]$^+$	19
133.879	133.879	15.2	[Cr_2(NO)]$^+$	0
119.876	119.876	43.9	[Cr_2O]$^+$	0
116.980	116.980	23.7	[Cr(cp)]$^+$	100
103.881	103.881	1.5	[Cr_2]$^+$	2
66.048	66.047	4.6	[C_5H_6]$^+$	6
65.040	65.039	4.6	[C_5H_5]$^+$	6
51.942	51.941	47.5	Cr^+	41

[a] ±0.001 mass unit. [b] The assignments involve the most abundant naturally occurring isotopes, *e.g.* ^{52}Cr, in each fragment. [c] From ref. 10; assignments are for the analogous fragments of [{Fe(cp)$(CO)_2$}$_2$].

The two compounds exhibit some chemical similarities, and these are summarized in equations (1)—(3) (M = Fe or Cr, L = C or N respectively). Thus, we find that

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[7] For the structure of the chromium dimer, see J. L. Calderon, S. Fontana, E. Frauendorfer, and V. W. Day, *J. Organometallic Chem.*, 1974, **64**, C10; for the *trans* structure of the iron dimer, see R. F. Bryan and P. T. Greene, *J. Chem. Soc.* (*A*), 1970, 3064.

[8] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc.* (*A*), 1970, 3068.

[9] R. M. Kirchner, T. J. Marks, J. S. Kristoff, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 6602 and refs. therein.

[10] J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, *J. Chem. Soc.* (*A*), 1966, 1663.

[11] *Cf.* H. Brunner, *J. Organometallic Chem.*, 1968, **14**, 173.

$[\{\mathrm{Cr(cp)(NO)_2}\}_2]$ is cleaved by iodine, hydrochloric acid, or nitrosyl chloride at ambient temperature with concurrent conversion of the bridging nitrosyl ligands into

$$[\{\mathrm{M(cp)(LO)_2}\}_2] + \mathrm{I_2} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{CHCl_3\ or}} 2[\mathrm{M(cp)(LO)_2I}] \qquad (1)$$

$$[\{\mathrm{M(cp)(LO)_2}\}_2] + 2\ \mathrm{HCl(aq)} \xrightarrow[\mathrm{O_2}]{\mathrm{ethanol}} 2[\mathrm{M(cp)(LO)_2Cl}] \qquad (2)$$

$$[\{\mathrm{M(cp)(LO)_2}\}_2] + 2\mathrm{NOCl} \xrightarrow{\mathrm{CH_2Cl_2}} 2[\mathrm{M(cp)(LO)_2Cl}] \qquad (3)$$

terminal nitrosyl ligands in a manner identical to that reported[4,5,12] for $[\{\mathrm{Fe(cp)(CO)_2}\}_2]$, the compounds $[\mathrm{Cr(cp)(NO)_2X}]$ ($\mathrm{X} = \mathrm{Cl}$ or I) being the final products. However, in other aspects of their chemistry the two dimers are significantly different.

Reduction of $[\{\mathrm{Fe(cp)(CO)_2}\}_2]$ by sodium amalgam in thf proceeds readily at room temperature, and virtually quantitative yields of the $[\mathrm{Fe(cp)(CO)_2}]^-$ anion can be obtained. In contrast, we find that the reduction of $[\{\mathrm{Cr(cp)(NO)_2}\}_2]$ under identical conditions leads rapidly to complete decomposition of the nitrosyl compound. The compound is unaffected by zinc amalgam in thf or benzene, and the anion $[\mathrm{Cr(cp)(NO)_2}]^-$ is unknown. Preliminary polarographic studies in our laboratory reveal that this anion may be formed under the conditions of the experiment, and hence we are presently attempting to prepare this and other organometallic nitrosyl anions electrochemically.

It is in their reactions with halogen-containing species that the two dimers most clearly show their chemical differences. For example, the chromium dimer abstracts all the chlorine ligands from tin tetrachloride under the conditions indicated in equation (4), whereas the iron dimer reacts with $\mathrm{SnCl_4}$ in inert solvents to form a compound containing a heteronuclear metal–metal bond and the compound $[\mathrm{Fe(cp)(CO)_2Cl}]$ [equation (5)].[13] The progress of reactions such as (4) can be

$$2[\{\mathrm{Cr(cp)(NO)_2}\}_2] + \mathrm{SnCl_4} \xrightarrow[\mathrm{reflux}]{\mathrm{thf}} 4[\mathrm{Cr(cp)(NO)_2Cl}] + \mathrm{Sn} \qquad (4)$$

$$[\{\mathrm{Fe(cp)(CO)_2}\}_2] + \mathrm{SnCl_4} \xrightarrow{\mathrm{reflux}} [\mathrm{Fe(cp)(CO)_2(SnCl_3)}] + [\mathrm{Fe(cp)(CO)_2Cl}] \qquad (5)$$

monitored very conveniently by i.r. spectroscopy since the characteristic absorptions due to nitrosyl groups of the reactant $[\{\mathrm{Cr(cp)(NO)_2}\}_2]$ occur at 1 667 (terminal) and 1 512 $\mathrm{cm^{-1}}$ (bridging) whereas those due to the two terminal nitrosyl groups of the product $[\mathrm{Cr(cp)(NO)_2Cl}]$ occur at 1 815 and 1 710 $\mathrm{cm^{-1}}$.

The propensity of the nitrosyl dimer to abstract halogen atoms dominates its reactions with inorganic and organometallic halides. Hence, treatment of $[\{\mathrm{Cr(cp)(NO)_2}\}_2]$ with the chlorides of bivalent mercury, tin, or lead results in the formation of the elemental metals and the customary $[\mathrm{Cr(cp)(NO)_2Cl}]$, *i.e.* as in equation (6) ($\mathrm{M} = \mathrm{Hg}$, Sn, or Pb). The iron carbonyl dimer, on

$$[\{\mathrm{Cr(cp)(NO)_2}\}_2] + \mathrm{MCl_2} \xrightarrow[\mathrm{reflux}]{\mathrm{thf\ or\ butan\text{-}1\text{-}ol}} 2[\mathrm{Cr(cp)(NO)_2Cl}] + \mathrm{M} \qquad (6)$$

the other hand, undergoes an oxidative-addition reaction with $\mathrm{SnCl_2}$ under comparable experimental conditions [equation (7)] to yield a product which contains covalent

$$[\{\mathrm{Fe(cp)(CO)_2}\}_2] + \mathrm{SnCl_2} \xrightarrow[\mathrm{reflux}]{\mathrm{butan\text{-}1\text{-}ol}} [\{\mathrm{Fe(cp)(CO)_2}\}_2\mathrm{SnCl_2}] \qquad (7)$$

iron–tin bonds,[14] and it apparently does not react with $\mathrm{PbCl_2}$.[8] Furthermore, $[\{\mathrm{Cr(cp)(NO)_2}\}_2]$ functions as a Wurtz coupling reagent when treated with appropriate organometallic halides, as illustrated in equations (8) and (9). Both conversions proceed smoothly in refluxing thf, but reaction (8) is hampered by the fact that $[\mathrm{Fe(cp)(CO)_2Cl}]$ is not particularly thermally stable under

$$[\{\mathrm{Cr(cp)(NO)_2}\}_2] + 2[\mathrm{Fe(cp)(CO)_2Cl}] \xrightarrow[\mathrm{reflux}]{\mathrm{thf}} [\{\mathrm{Fe(cp)(CO)_2}\}_2] + 2[\mathrm{Cr(cp)(NO)_2Cl}] \qquad (8)$$

the experimental conditions employed. Interestingly, if $[\mathrm{Fe(cp)(CO)_2I}]$ is used in place of its chloro-analogue

$$[\{\mathrm{Cr(cp)(NO)_2}\}_2] + 2[\mathrm{Mn(CO)_5Cl}] \xrightarrow[\mathrm{reflux}]{\mathrm{thf}} [\mathrm{Mn_2(CO)_{10}}] + 2[\mathrm{Cr(cp)(NO)_2Cl}] \qquad (9)$$

in reaction (8), or if reaction (8) is allowed to proceed at room temperature for 8 d, detectable amounts of $[\{\mathrm{Fe(cp)(CO)_2}\}_2]$ are not formed despite the fact that halogen abstraction by the chromium nitrosyl dimer still occurs. Similarly, when $[\mathrm{W(cp)(NO)_2Cl}]$ is treated with $[\{\mathrm{Cr(cp)(NO)_2}\}_2]$ in thf at reflux in the usual 2 : 1 stoicheiometry the expected $[\mathrm{Cr(cp)(NO)_2Cl}]$ is formed in good yields, but no nitrosyl-containing complexes of tungsten (such as the unknown $[\{\mathrm{W(cp)(NO)_2}\}_2]$) can be detected in the final reaction mixture.

The reaction between the chromium dimer and $\mathrm{SnPh_3Cl}$ in refluxing thf [equation (10)] is novel. The two chromium-containing products are formed in approximately equal amounts, and it is clear that halogen abstraction by the nitrosyl reagent has again occurred. The exact nature of the tin product remains to be ascer-

$$[\{\mathrm{Cr(cp)(NO)_2}\}_2] + \mathrm{SnPh_3Cl} \xrightarrow[\mathrm{reflux}]{\mathrm{thf}} \{\mathrm{Sn}\} + [\mathrm{Cr(cp)(NO)_2Cl}] + [\mathrm{(ON)(cp)Cr(\mu\text{-}NO)(\mu\text{-}NH_2)Cr(cp)(NO)}] \qquad (10)$$

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[12] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 38.

[13] R. C. Edmondson and M. J. Newlands, *Chem. and Ind.*, 1966; 1888; R. C. Edmondson, E. Eisner, M. J. Newlands, and L. K. Thompson, *J. Organometallic Chem.*, 1972, **35**, 119.

[14] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179.

tained, but it is *not* hexaphenyldistannane. The binuclear chromium compound, $[Cr_2(cp)_2(NO)_3(NH_2)]$, was first obtained[15] as a by-product (1% yield) during the preparation of $[\{Cr(cp)(NO)_2\}_2]$, and it was presumed to be formed by the unusual reduction of a Cr–NO linkage in the latter compound to a $Cr–NH_2$ group by the $Na[BH_4]$ employed. Indeed, the molecular structure of the amido-complex in the solid state[16] closely resembles that exhibited by $[\{Cr(cp)(NO)_2\}_2]$, the amido-group simply replacing one of the bridging nitrosyl groups. Infrared, ^1H n.m.r., and mass spectral data are in accord with this structure,[15] but the 70-eV mass spectrum based on the high-resolution data presented in Table 3, gives a slightly different interpretation. Contrary to the original report, we assign the peaks at *m/e* **249.952** and **132.998** to the ions $[Cr_2(cp)_2O]^+$ and $[Cr(cp)(NH_2)]^+$ respectively. Generally, the fragmentation pattern of the amido-compound is quite similar to that noted for $[\{Cr(cp)(NO)_2\}_2]$ (Table 2) as again the sequential loss of nitrosyl groups, the intermetallic migration of the cyclopentadienyl group, the preponderance of bimetallic ions, and the symmetrical fission of the molecule are observed. However, the most abundant species present in this case is $[Cr(cp)_2]^+$, and the novel nitride-containing ion $[Cr_2(cp)N]^+$ is observed whereas such nitride ions are not detectable in the mass spectrum of $[\{Cr(cp)(NO)_2\}_2]$.

TABLE 3

High-resolution mass spectral data for $[Cr_2(cp)_2(NO)_3(NH_2)]$

m/e		Relative	
Found[a]	Calc.	abundance	Assignment[b]
339.972	339.972	60.5	$[Cr_2(cp)_2(NO)_3(NH_2)]^+$
309.970	309.974	52.6	$[Cr_2(cp)_2(NO)_2(NH_2)]^+$
279.980	279.983	25.4	$[Cr_2(cp)_2(NO)(NH_2)]^+$
263.957	263.957	7.1	$[Cr_2(cp)_2(NO)]^+$
249.952	249.954	42.2	$[Cr_2(cp)_2O]^+$
214.937	214.937	22.6	$[Cr_2(cp)(NO)(NH_2)]^+$
200.934	200.934	86.4	$[Cr_2(cp)(NH_2)O]^+$
184.914	184.915	25.0	$[Cr_2(cp)O]^+$
182.921	182.923	8.9	$[Cr_2(cp)N]^+$
182.017	182.019	100.0	$[Cr(cp)_2]^+$
135.892	135.895	5.5	$[Cr_2(NH_2)O]^+$
132.998	132.998	12.7	$[Cr(cp)(NH_2)]^+$
116.979	116.980	17.1	$[Cr(cp)]^+$
66.047	66.047	5.5	$[C_5H_6]^+$
65.039	65.039	4.4	$[C_5H_5]^+$
51.939	51.941	28.2	Cr^+

[a] ±0.001 mass unit. [b] The assignments involve the most abundant naturally occurring isotopes, *e.g.* ^{52}Cr, in each fragment.

The origin of the bimetallic amido-compound in reaction (10) remains uncertain at the present time, but it is of interest to note that the same compound can be obtained in 15% yield by heating a toluene solution of $[\{Cr(cp)(NO)_2\}_2]$ under gentle reflux for 24 h. (The principal product in this latter reaction is a red-brown cluster compound whose exact formulation has yet to be determined.) Consequently, even though $[\{Cr(cp)(NO)_2\}_2]$ is not detectably changed by refluxing in thf for 24 h, it is possible that during the prolonged time (8 d) required to effect completion of reaction (10) some thermal conversion into $[Cr_2(cp)_2(NO)_3(NH_2)]$ may have occurred.

In reactions with halogen-containing organic compounds, $[\{Cr(cp)(NO)_2\}_2]$ again exhibits its tendency to abstract halogen atoms. For example, it smoothly converts vicinal dihalides into olefins in refluxing thf, the rate of halogen abstraction increasing in the order I < Br < Cl. This observation suggests that this tendency of the dimer may well be of some utility in organic synthesis. Furthermore, the utility could be enhanced by regenerating the dimer *in situ* by direct reduction of the $[Cr(cp)(NO)_2X]$ (X = halide) product by zinc amalgam. Further investigations are in progress.

The Pyrolysis of $[\{Mn(C_5H_4Me)(CO)(NO)\}_2]$.—In view of the reactions of $[\{Cr(cp)(NO)_2\}_2]$ and $[\{Fe(cp)(CO)_2\}_2]$ considered previously in this paper, we were interested in determining how the related manganese dimer, $[\{Mn(C_5H_4Me)(CO)(NO)\}_2]$, reacts with halogen-containing reactants under comparable experimental conditions. Unfortunately, the manganese compound is quite thermally labile and it reacts with $SnCl_2$ in refluxing thf to produce only intractable decomposition products which do not contain carbonyl or nitrosyl ligands. In fact, the dimer itself readily decomposes in refluxing thf and is converted in low yields into $[Mn(C_5H_4Me)(CO)_3]$ and $[Mn_3(C_5H_4Me)_3(NO)_4]$ as the only detectable organometallic carbonyl and nitrosyl products.

The new trimetallic compound $[Mn_3(C_5H_4Me)_3(NO)_4]$ forms black crystals which are freely soluble in common organic solvents (except the paraffin hydrocarbons) to give air-stable green-black solutions. When heated in an open capillary the crystals begin to decompose at 157 ± 2 °C. The ^1H n.m.r. spectrum of the compound in $CDCl_3$ consists of two sharp resonances at τ 5.22 and 8.17 of relative intensity 4 : 3, thereby indicating the equivalence of the three methylcyclopentadienyl rings and the diamagnetism of the compound. The i.r. spectrum in dichloromethane exhibits three strong bands at 1 538, 1 483, and 1 333 cm^{-1} attributable to bridging nitrosyl groups. The major peaks in the mass spectrum of the compound are due to the ions $[Mn_3(C_6H_7)_3(NO)_x]^+$ (x = 4, 2, or 1) and $[Mn_2(C_6H_7)_2(NO)_y]^+$ (y = 2 or 1), the $[Mn_3(C_6H_7)_3(NO)]^+$ ion being the most abundant. The compound is thus apparently isostructural with its cyclopentadienyl analogue, $[Mn_3(cp)_3(NO)_4]$, which possesses three doubly bridging nitrosyl groups and one triply bridging nitrosyl group.[17]

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