Organometallic Nitrosyl Chemistry. Part II.[1] Alkyl- and Aryl-(η-cyclopentadienyl)dinitrosyl Complexes of Chromium, Molybdenum, and Tungsten

By **James K. Hoyano, Peter Legzdins,*** and **John T. Malito,** Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1W5

Reactions of organoaluminium reagents with the chloro-complexes [(cp)M(NO)$_2$Cl] (M = Cr, Mo, or W; cp = η-cyclopentadienyl) in benzene solution give the corresponding alkyl or aryl complexes [(cp)M(NO)$_2$R] (R = Me, Et, Bu^t, or Ph) in good yields. The factors affecting the success of this preparative route and the properties of these new organometallic products are discussed. A novel high-yield synthesis of [{(cp)Cr(NO)$_2$}$_2$] is also described.

Since the initial discovery of σ-bonded alkyl and aryl transition-metal complexes, the criteria for their stability have evolved considerably. This evolution has, in turn, resulted in the recent preparation and characterization of a number of complexes which were originally believed to be so unstable as to be unisolable under ambient conditions. Indeed, it now appears that many previous attempts to synthesize metal complexes containing single bonds to a saturated carbon atom failed only because of unsuitable reaction conditions and not because of any inherent instability of the metal–carbon bonds.[2,3]

As an extension of our recent work [1] on the synthesis of chloronitrosyl derivatives of the Group 6 metals, we report in this paper a quite general method for the preparation of thermally stable complexes of the type [(cp)M(NO)$_2$R] (M = Cr, Mo, or W; R = alkyl or aryl; cp = η-cyclopentadienyl). Although some of the chromium complexes were first reported[4] in 1956, the molybdenum and tungsten analogues cannot be synthesized in an identical manner and have thus remained unknown until the present time. This study on the preparation of various [(cp)M(NO)$_2$R] derivatives has also afforded a high-yield synthesis of [{(cp)Cr(NO)$_2$}$_2$].

EXPERIMENTAL

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

I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1 601 cm^{-1} band of polystyrene film. ^{1}H N.m.r. spectra were recorded on a Varian Associates T60 spectrometer with tetramethylsilane being employed as internal standard. Mass spectra were recorded at 70 eV † on Atlas CH4B or Associated Electrical Industries MS902 spectrometers, using the direct-probe-insertion method with the assistance of Mr. G. Eigendorf and Mr. G. Gunn. Elemental analyses were carried out by Mr. P. Borda of this department.

Because the procedures for the preparation of the various alkyl and aryl derivatives were quite similar, two representative syntheses are described below and particular reaction and isolation conditions are summarized in Table 1. The Table also presents the physical properties and analytical data for all the products. The requisite starting chlorides [(cp)M(NO)$_2$Cl] were prepared as previously described.[1]

(η-Cyclopentadienyl)methyldinitrosyltungsten, [(cp)W(NO)$_2$Me].—A benzene solution of Me$_3$Al (12·0 cm^3 of a 0·26M † solution, 3·10 mmol) was added dropwise during 30 min to a stirred solution of [(cp)W(NO)$_2$Cl] (1·00 g, 2·90 mmol) in the same solvent (25 cm^3) at room temperature. The resulting green solution was stirred for 48 h. (This reaction can be conveniently monitored by i.r. spectroscopy and such monitoring of several runs showed this to be the optimum stoicheiometry and reaction time.) At the end of this time, a red-brown solid had deposited on the sides of the reaction flask, and an i.r. spectrum of the supernatant green solution indicated that it contained approximately equimolar amounts of the desired [(cp)-

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† 1 eV ≈ 1·60 × 10^{-19} J, 1M = 1 mol dm^{-3}.

[1] Part I, P. Legzdins and J. T. Malito, *Inorg. Chem.*, submitted for publication.

[2] G. Wilkinson, *Science*, 1974, **185**, 109.

[3] For general reviews on the syntheses and properties of σ-bonded carbon–metal complexes see G. W. Parshall and J. J. Mrowca, *Adv. Organometallic Chem.*, 1968, **7**, 157; P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, **2**, 271; F. Calderazzo, *Pure Appl. Chem.*, 1973, **33**, 453; M. C. Baird, *J. Organometallic Chem.*, 1974, **64**, 289.

[4] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

W(NO)$_2$Me] and unchanged $[(cp)W(NO)_2Cl]$ [as judged by relative ν(NO) band intensities]. The final reaction mixture was filtered and the filtrate was concentrated to *ca.* 15 cm^3. This solution was chromatographed on a short (3 × 7 cm) alumina column with benzene as eluant. The green band was collected and evaporated to dryness under reduced pressure to give the pale green solid product. Sublimation of this solid at 30 °C (0·005 mmHg) onto a water-cooled probe yielded *crystals* of analytically pure $[(cp)W(NO)_2Me]$ (0·20 g, 21%).

TABLE 1

Reaction conditions, purification methods, and physical and analytical data for the $[(cp)M(NO)_2R]$ complexes

Complex	Alkylating or arylating agent	Reaction t/h	Purification methods [a]	Colour	M.p. (θ_c/°C)	Analyses/% Found C	H	N	Calc. C	H	N
$[(cp)Cr(NO)_2Ph]$ [b]	Ph_3Al	0·5	(i), (ii)	Dark green	48—48·5 [c]	52·05	4·10	10·95	51·95	3·95	11·0
$[(cp)Cr(NO)_2Me]$ [b]	Me_3Al	0·5	(i), (ii)	Dark green	80·5—81·0	37·4	4·20	14·5	37·5	4·20	14·6
$[(cp)Cr(NO)_2Et]$ [b]	Et_3Al	0·5	(i)	Green	Oil	40·75	4·90	13·45	40·8	4·90	13·6
$[(cp)Cr(NO)_2Bu^i]$	Bu^i_2AlH	0·5	(i)	Green	Oil	46·5	6·20	11·6	46·15	6·05	11·95
$[(cp)Mo(NO)_2Ph]$	Ph_3Al	1·5	(i)	Olive-green	Oil	44·3	3·45	9·15	44·3	3·40	9·40
$[(cp)Mo(NO)_2Me]$	Me_3Al	1	(i)	Green	61·5—62·0	30·7	3·35	11·8	30·55	3·40	11·85
$[(cp)Mo(NO)_2Et]$	Et_3Al	1	(i)	Green	Oil	34·05	4·40	10·9	33·6	4·05	11·2
$[(cp)Mo(NO)_2Bu^i]$	Bu^i_2AlH	0·5	(i)	Green	Oil	39·35	5·25	10·05	38·85	5·05	10·05
$[(cp)W(NO)_2Ph]$	Ph_3Al	1	(i), (ii)	Green	109—110	34·4	2·75	7·05	34·2	2·60	7·25
$[(cp)W(NO)_2Me]$	Me_3Al	48	(i), (ii)	Pale green	75—76	22·55	2·40	8·60	22·25	2·50	8·65

[a] (i), Chromatographic separation on alumina using benzene as eluant; (ii) sublimation *in vacuo*. [b] Previously reported and synthesized by reaction of a Grignard reagent on the appropriate bromide or iodide, see ref. 4. [c] Originally reported as a green oil in ref. 4.

(*η-Cyclopentadienyl*)*dinitrosylphenylmolybdenum*, $[(cp)Mo(NO)_2Ph]$.—The solid Ph_3Al (0·35 g, 1·36 mmol) was dissolved in warm benzene (40—50 °C, 70 cm^3). This solution was added dropwise during 30 min to a solution of $[(cp)Mo(NO)_2Cl]$ (1·00 g, 3·91 mmol) in benzene at room temperature. A red-brown solid precipitated immediately. After complete addition of the aluminium reagent, the reaction mixture was stirred for 1 h at which point an i.r. spectrum of the supernatant green solution exhibited no nitrosyl absorptions attributable to the starting chloride. The benzene solution was decanted from the reaction mixture, concentrated under reduced pressure to *ca.* 20 cm^3, and then chromatographed on an alumina column. Elution with benzene (80 cm^3) gave a green solution from which the solvent was removed *in vacuo* to obtain an olive-green oil. This oil was rechromatographed on alumina with benzene as eluant and only the main portion of the product band was collected. Solvent was removed from the eluate under high vacuum (<0·005 mmHg) for 4 h and the olive-green *oil* thus obtained was an analytically pure sample of $[(cp)Mo(NO)_2Ph]$ (0·65 g, 56%).

All the new complexes shown in Table 1 (typically obtained in yields of 30—50%) are stable in air for short periods of time and appear to be stable for long periods in an atmosphere of prepurified nitrogen. Some of the molybdenum and tungsten derivatives exhibit erratic behaviour in air. For example, some samples of $[(cp)W(NO)_2Ph]$ are stable in air for days while others decompose in less than 1 h. In solution the various alkyl and aryl derivatives decompose rapidly when exposed to air, especially in non-polar solvents such as benzene. The qualitative air-stability of these complexes appears to diminish in the order Cr > Mo > W.

Bis[(*η-cyclopentadienyl*)*dinitrosylchromium*], $[\{(cp)Cr(NO)_2\}_2]$.—A zinc amalgam was prepared by stirring zinc shot (2 g) with mercury (100 g) until all the zinc dissolved. This amalgam was stirred with a solution of $[(cp)Cr(NO)_2Cl]$ (4·50 g, 21·2 mmol) in tetrahydrofuran (thf, 50 cm^3) at room temperature. The reaction was again monitored by i.r. spectroscopy and was allowed to proceed until the nitrosyl absorptions due to the starting chloro-complex had completely disappeared. An optimum reaction time was thus found to be 21 h; continued stirring of the reaction mixture beyond this time resulted in lower yields of the desired product. The thf solution was then decanted from the amalgam and was filtered. The filtrate was taken to dryness *in vacuo* and the resulting residue was chromatographed on an alumina column with benzene as eluant. The dark red-violet band was collected and was taken to dryness *in vacuo* to obtain 2·90 g (75%) of analytically pure $[\{(cp)Cr(NO)_2\}_2]$ (Found: C, 33·8; H, 3·05; N, 15·4. Calc. for $C_{10}H_{10}Cr_2N_4O_4$: C, 33·9; H, 2·85; N, 15·8%).

RESULTS AND DISCUSSION

All the complexes in Table 1 were prepared in reasonable yields by reaction of the corresponding chloro-complexes with organoaluminium reagents according to the general equation (1) where M = Cr, Mo, or W and

$$[(cp)M(NO)_2Cl] + R{-}Al\!< \xrightarrow{\text{benzene}} [(cp)M(NO)_2R] + Cl{-}Al\!< \quad (1)$$

R = alkyl or aryl. (The exact nature of the aluminium product remains to be ascertained.) For M = Cr or Mo, the reaction appears to be quite general and its practical applicability is limited only by the availability of the appropriate R_3Al reagent. Interestingly, when Bu^i_2AlH was used in reaction (1) with the chromium or molybdenum halides, the alkyl group was preferentially transferred to the transition metal. When M = W and Me_3Al was used as the alkylating agent, reaction (1) proceeded very slowly and did not reach completion even in 48 h. Similar reactions involving Et_3Al and Bu^i_2AlH with the tungsten halide under various reaction conditions gave no detectable alkylated products.

The i.r., ^1H n.m.r., and mass-spectral data (summarized in Tables 2 and 3) indicate that all of the isolated $[(cp)M(NO)_2R]$ complexes contain the alkyl or aryl ligand attached by a metal–carbon single bond. The i.r. spectra of the complexes exhibited two strong bands in the terminal nitrosyl-stretching region of 1 600—1 800 cm^{-1}. As expected, for a given metal, the nitrosyl-stretching frequencies shifted to lower values in going from the chloro- to the aryl derivative and finally to the alkyl species. The ^{1}H n.m.r. spectra all showed sharp singlets for the cp protons and the expected patterns and integration ratios for the alkyl and aryl protons. The presence of the σ-bonded ethyl group in the [(cp)Mo(NO)$_2$Et] complex was confirmed by computer fitting of the complex A_2B_3 multiplet in the alkyl proton region * and the following spectral parameters can thus be extracted: $\tau(CH_2)$ 8·10, $\tau(CH_3)$ 8·26, $J(CH_2,CH_3)$ 7·54 Hz. A somewhat surprising feature of the n.m.r. spectra is that for a given metal the position of the cp resonance changed very little in going from the chloro- to the aryl to the alkyl complex.

TABLE 2

I.r. and ^{1}H n.m.r. data for the [(cp)M(NO)$_2$R] complexes

Complex	I.r.,[a] $\bar{\nu}$(NO)/cm^{-1}		N.m.r.[b]	
			τ(cp)	τ (others)
[(cp)Cr(NO)$_2$Cl] [c]	1 815s	1 710vs [d]	5·22	
[(cp)Cr(NO)$_2$Ph]	1 792	1 690	5·27	2·7(m) [e]
[(cp)Cr(NO)$_2$Me]	1 780	1 675	5·63	9·55 (singlet CH$_3$)
[(cp)Cr(NO)$_2$Et]	1 772	1 670	5·45	8·6(m)
[(cp)Cr(NO)$_2$Bu^i]	1 775	1 675	5·33	8—9(m)
[(cp)Mo(NO)$_2$Cl] [c]	1 758	1 665 [d]	4·93	
[(cp)Mo(NO)$_2$Ph]	1 745	1 658	4·90	2·7(m)
[(cp)Mo(NO)$_2$Me]	1 728	1 640	4·92	9·20 (singlet CH$_3$)
[(cp)Mo(NO)$_2$Et]	1 735	1 643	4·90	8·2(m)
[(cp)Mo(NO)$_2$Bu^i]	1 725	1 638	4·93	7·6—8·8(m)
(cp)W(NO)$_2$Cl] [c]	1 733	1 650 [d]	5·02	
[(cp)W(NO)$_2$Ph]	1 713	1 630	4·95	2·6(m)
[(cp(W(NO)$_2$Me]	1 705	1 620	4·98	8·82 (singlet CH$_3$)

[a] Hexane solution unless indicated otherwise. [b] C_6D_6 Solution. [c] These complexes are more fully described in ref. 1. [d] Dichloromethane solution. [e] Approximate centroid of complex multiplet (m).

TABLE 3

Mass-spectral fragmentation data for the [(cp)M(NO)$_2$R] complexes [a]

Complex	Ion [b]							
	M$^+$	[(cp)M]$^+$	[(cp)M(NO)]$^+$	[(cp)M(NO)$_2$]$^+$	[(C$_3$H$_3$)MR]$^+$	[(cp)MR]$^+$	[(cp)M(NO)R]$^+$	[(cp)M(NO)$_2$R]$^+$
[(cp)Cr(NO)$_2$Ph]	10·0	8·3				2·3	7·5	0·7
[(cp)Mo(NO)$_2$Ph]					2·7	3·6	8·2	3·6
[(cp)W(NO)$_2$Ph]		1·7			4·2	7·2	10·0	5·6
[(cp))Cr(NO)$_2$Me]	10·0	8·4	2·7	1·2		2·1	7·2	1·6
[(cp)Mo(NO)$_2$Me]	5·7	3·6	10·0	6·2			6·2	6·0
[(cp)W(NO)$_2$Me]	0·4		2·9	3·4			4·6	6·2

[a] Entries are relative-ion intensities with the most intense metal-containing ion assigned an arbitrary value of 10·0. Relative intensities were evaluated by measuring peak heights corresponding to the most abundant isotope of each metal: ^{52}Cr, ^{98}Mo, and ^{184}W. [b] Only unambiguously assignable ions are given; for the polyisotopic molybdenum and tungsten, overlapping of some medium to strong intensity peaks in the lower mass range made assignments difficult. Spectra of selected complexes were recorded on the MS902 high-resolution instrument which measured exact masses of all major peaks; calculated and measured values were in good agreement.

The mass spectrum of each complex exhibited the molecular ion as the highest-mass fragment. Fragmentation patterns were similar for all complexes; the main fragments and their relative intensities for the phenyl and methyl derivatives are shown in Table 3. The ethyl and isobutyl complexes showed similar fragments but their mass spectra were complicated by concomitant fragmentation of the alkyl groups. Table 3 clearly displays the principal similarities and differences in the fragmentation patterns of the various complexes. All the complexes showed the molecular ion and ions corresponding to stepwise loss of the nitrosyl ligands. The alkyl derivatives exhibited competing NO and R group loss from the molecular ion whereas the phenyl derivatives showed no peaks corresponding to [(cp)M(NO)]$^+$ or [(cp)M(NO)$_2$]$^+$. This observation suggests that a stronger metal–carbon bond exists in the phenyl complexes. The major difference among the metals is that all the chromium-containing complexes showed very strong peaks corresponding to Cr$^+$ and [(cp)Cr]$^+$ whereas for the molybdenum- and tungsten-containing complexes the corresponding peaks were relatively weak or not observed. For the latter complexes, peaks corresponding to the higher-mass fragments were more intense.

The preceding discussion of the properties of the new tungsten and molybdenum complexes indicates that once they are formed they are quite stable. It thus appears that previous attempts [5] to prepare these species did not succeed solely because of the reaction conditions employed. Our studies in this regard will now be more fully discussed.

Organoaluminium reagents are known to be particularly mild alkylating agents,[6] a feature that is well illustrated by the exclusive monoalkylation of some dichlorides of ruthenium even when an excess of the organoaluminium reagent is used at elevated temperatures.[7] We find that these milder reactants must be employed if reaction (1) is to succeed. The use of more powerful alkylating agents such as RLi or RMgX in reaction (1) under a variety of conditions failed to give even spectroscopically detectable amounts of the alkylated products when M = Mo or W. The chromium analogues can be prepared by the Grignard method,[4] but the yields are substantially lower than those obtained when organoaluminium reagents are employed. It thus

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* We thank Ms. V. Gibb for carrying out these computations.

[5] R. B. King, *Inorg. Chem.*, 1968, **7**, 90.

[6] P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209.

[7] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1963, 6017.

appears that the less selective alkylating or arylating agents attack other functional groups in addition to the chloro-ligand.

A commonly employed synthetic route to σ-bonded alkyl and aryl complexes is the reaction of a transition-metal anion with the appropriate alkyl or aryl halide.[3,8] This avenue to complexes of the type described in this paper has been thwarted because the anions $[(cp)M(NO)_2]^-$ have not yet been prepared. {Indeed, the only well characterized organometallic nitrosyl anion which has been used successfully in synthesis is $[Fe(CO)_3(NO)]^-$.}[9-11] We found that attempts to reduce the chlorides $[(cp)M(NO)_2Cl]$ with sodium amalgam resulted in complete decomposition of all three complexes. Similarly, reduction with magnesium or zinc amalgam decomposed the tungsten and molybdenum chloro-complexes. Interestingly, however, treatment of $[(cp)Cr(NO)_2Cl]$ in thf with a zinc amalgam afforded an efficient preparative route to $[\{(cp)Cr(NO)_2\}_2]$, *i.e.* as in (2). This dimeric chromium complex has been previously obtained in low yields ($<5\%$) by reduction of the chloro-complex with sodium tetrahydroborate in a two-phase water–benzene system.[12] Yields of 30—50% of $[\{(cp)Cr(NO)_2\}_2]$ were also obtained when finely divided magnesium or ytterbium metal was employed in reaction (2) instead of the zinc amalgam. In these latter reactions we have not obtained any evidence for the existence of activated species[13] such as '$[(cp)(NO)_2CrMgCl]$.' Similar reactions of the tungsten and molybdenum chloro-complexes with the powdered metals led only to eventual decomposition. Consequently the dimeric complexes $[\{(cp)M(NO)_2\}_2]$ (M = Mo or W) still remain unknown.

$$[(cp)Cr(NO)_2Cl] + Zn/Hg \xrightarrow{\text{thf}} [\{(cp)Cr(NO)_2\}_2]\ (75\%) \qquad (2)$$

Another possible synthetic route to these dimeric complexes might involve the presently unknown hydrides $[(cp)M(NO)_2H]$ which under certain conditions could possibly thermally decompose to the desired products. Indeed, such a hydrido-intermediate has been suggested for the tetrahydroborate reduction of $[(cp)Cr(NO)_2Cl]$.[12] We found that attempts to prepare these hydrides by treatment of the molybdenum and tungsten chlorides with either $Li[AlH_4]$, $Na[BH_4]$, $Me_3N{\cdot}AlH_3$, or Ph_3SnH failed. Another potential preparative path to the hydrides might involve olefin elimination from an alkyl complex such as $[(cp)Mo(NO)_2Et]$. Such reactions and other aspects of the chemistry of these novel alkyl and aryl complexes are currently under investigation.

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

[13] For a discussion of transition-metal halide activated species see A. E. Crease and P. Legzdins, *J.C.S. Chem. Comm.*, 1973, 775; A. E. Crease, P. Legzdins, and E. R. Sigurdson, *Ann. New York Acad. Sci.*, 1974, **239**, 129.