Organometallics **1990,** *9,* 431–439

perature factors of the hydrogen atoms were set to 1.3 times the temperature factors of the carbons to which they were bonded.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, bond distances, and bond angles for 5 and 7 (14 pages); tables of structure factor amplitudes for 5 and 7 (23 pages). Ordering information is given on any current masthead page.

Regiospecific Condensation of Methyl Propiolate with 2,3-Dimethyl-2-butene Mediated by the Electrophilic η^5-Cyclopentadienyl Dinitrosyl Tetrafluoroborate Salts of the Group 6 Metals[1,2]

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Chloride abstraction from $Cp'M(NO)_2Cl$ (Cp' = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5); M = Cr, Mo, W) with an equimolar amount of $AgBF_4$ in CH_2Cl_2 generates reactive solutions of $Cp'M(NO)_2BF_4$. During their reactions with various nucleophiles, the $Cp'M(NO)_2BF_4$ compounds behave as though they are the formally 16-electron cations $Cp'M(NO)_2^+$. Thus, all the $CpM(NO)_2BF_4$ complexes abstract a phenyl group from the BPh_4^- anion to form the known $CpM(NO)_2Ph$ compounds, and $CpW(NO)_2BF_4$ catalyzes the oligomerization of 2-methylpropene. Furthermore, methyl propiolate and 2,3-dimethyl-2-butene condense regiospecifically in the coordination spheres of all the $Cp'M(NO)_2^+$ cations to produce the cationic lactone complexes $[Cp'M(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(OMe)]^+$. All the cationic lactone complexes undergo facile *O*-demethylation reactions upon exposure to an acetone solution of NaI. The resulting η^1-lactone-containing organometallic compounds, $Cp'M(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)$, have all been fully characterized by conventional spectroscopic techniques, and a single-crystal X-ray crystallographic analysis has been performed on the CpMo member of this series of complexes. Crystal data for $CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)$: a = 11.337 (6) Å, b = 12.564 (3) Å, c = 11.958 (6) Å, β = 115.12 (4)°, Z = 4, space group $P2_1/c$, number of unique reflections 2713, number of variables 245, R_F = 0.021, R_{wF} = 0.030. The compound possesses a normal three-legged piano-stool molecular geometry, the intramolecular dimensions of the lactone ligand indicating the existence of some internal delocalization of π-electron density. Treatment of the neutral CpMo lactone complex with $[Me_3O]BF_4$ regenerates its cationic organometallic precursor, and treatment with iodine liberates the iodolactone from the molybdenum's coordination sphere. Interestingly, exposure of the neutral tungsten lactone complexes to air results in their being cleanly converted to the corresponding dioxo derivates $Cp'W(O)_2(\eta^1$-lactone).

Introduction

Transition-metal organometallic compounds continue to be widely exploited for effecting various specific organic transformations.[5] A principal reason for this state of affairs is that many catalytic and stoichiometric reactions resulting in the production of new organic compounds proceed only in the presence of a reactive organometallic fragment.[6] The large majority of the organometallic fragments employed during such reactions have involved carbonyl-containing species.[6] In principle, the related nitrosyl complexes should also be capable of functioning as specific reactants or selective catalysts for various organic conversions. However, the synthetic utility of these latter species has to date been relatively little exploited despite the fact that there is now a considerable number of organometallic nitrosyl complexes available.[7] One of the main differences between the two types of compounds is that the presence of the more electron-withdrawing NO

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(1) Organometallic Nitrosyl Chemistry. 41. Part 40: Herring, F. G.; Legzdins, P.; Richter-Addo, G. B. *Organometallics* **1989**, *8*, 1485.

(2) Taken in part from: Richter-Addo, G. B. Ph.D. Dissertation, The University of British Columbia, 1988.

(3) (a) The University of British Columbia. (b) Simon Fraser University.

(4) Author to whom correspondence concerning the crystallographic study should be addressed.

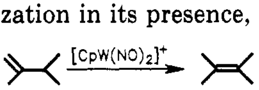
(5) For a recent review of the applications of transition-metal organometallic compounds to organic synthesis, see: Hegedus, L. S. *J. Organomet. Chem.* **1989**, *360*, 409 and references cited therein.

(6) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: New York, 1982.

(7) Richter-Addo, G. B.; Legzdins, P. *Chem. Rev.* **1988**, *88*, 991.

0276-7333/90/2309-0431$02.50/0

ligands[8] should impart more of an electrophilic character to the metal center in the nitrosyl complex than it would possess in the analogous carbonyl compound.[9] Indeed, our preliminary studies a few years ago of $CpW(NO)_2BF_4$ indicated that its characteristic chemistry in CH_2Cl_2 is dominated by its pronounced electrophilic character. For instance, 2,3-dimethyl-1-butene undergoes a rapid double-bond isomerization in its presence, i.e.



this transformation probably occurring via the electrophile-induced formation of an incipient carbocation.[10] More recently, we have established that the nitrosyl ligands play a profound role in establishing the physical and chemical properties of anionic and neutral radical complexes containing $CpM(NO)_2$ groups (M = Cr, Mo, W).[11] Consequently, we decided to embark on a more extensive study of the chemistry of the formally 16-electron $Cp'M(NO)_2^+$ cations (Cp' = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5); M = a group 6 metal) as they occur in their tetrafluoroborate salts with a view to developing the compounds containing them as useful (and possibly unique) reagents for organic synthesis.

In this paper we first describe some reactions of the $Cp'M(NO)_2^+$ cations as their BF_4^- salts that further delineate their electrophilic character. We then describe in detail the utilization of these cations for the synthesis of the complete series of six cationic lactone complexes $[Cp'M(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(OMe)]^+$ (Cp' = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5); M = Cr, Mo, W) by their regiospecific mediation of the reaction between methyl propiolate and 2,3-dimethyl-2-butene, which involves concomitant metal–carbon, carbon–oxygen, and carbon–carbon bond formation. Furthermore, we present details of the *O*-demethylation of these six cationic species to their neutral $Cp'M(NO)_2(\eta^1$-lactone) derivatives, from which the lactone ligands may be liberated by treatment with iodine. We also describe how exposure of both neutral lactone complexes of tungsten to air leads to their being cleanly converted to the corresponding dioxo derivatives. Finally, we present complete characterization data for all the new organometallic complexes isolated during this work (including a single-crystal X-ray crystallographic analysis of $CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O))$ and consider the implications of this study for the synthesis of new types of organic compounds.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous conditions under an atmosphere of dinitrogen unless specified otherwise. General procedures routinely employed in these laboratories have been described in detail previously.[12] Methyl propiolate (99%), 2,3-dimethyl-2-butene (98%), $AgBF_4$, $NaBPh_4$ (Gold Label), and $[Me_3O]BF_4$ were purchased from the Aldrich Chemical Co. and were used without further purification. 2-Methylpropene (CP grade) was purchased from the Matheson Gas Co. The $CpM(NO)_2Cl$ compounds (M = Cr, Mo, W)[13] and $Cp^*W(NO)_2Cl$[10] were prepared by published procedures. The $Cp^*M(NO)_2Cl$ complexes for M = Cr, Mo were synthesized in a manner similar to that employed for the congeneric tungsten species,[10] and their purity was established by elemental analyses. Preparatory gas chromatography was performed on a Varian Model 90-P gas chromatograph using an 8 ft × 0.125 in. column packed with 3% OV-17 on Supelcoport, and GC–MS samples were run with use of a DB-1 capillary column on a Varian Vista 6000 gas chromatograph interfaced with a Nermag R10-10 quadrupole mass spectrometer with the assistance of Dr. G. K. Eigendorf.

Generation of Dichloromethane Solutions of $Cp'M(NO)_2BF_4$ (Cp' = Cp, Cp*; M = Cr, Mo, W). Solutions of these complexes were prepared by treating CH_2Cl_2 solutions of their $Cp'M(NO)_2Cl$ precursors with equimolar amounts of solid $AgBF_4$ in the manner described in detail previously for $CpW(NO)_2BF_4$.[10] The chloride-abstraction reactions took from 15 to 45 min to go to completion, their progress being monitored by IR spectroscopy. This monitoring indicated that each conversion was clean, and hence it was assumed to be quantitative in each case. The final reaction mixtures were filtered through medium-porosity frits to remove the precipitated AgCl, and the green to brown filtrates were then treated with the appropriate organic substrates as described below.

Reaction of $CpW(NO)_2BF_4$ with 2-Methylpropene. To a cold (−10 °C) green dichloromethane solution (40 mL) of $CpW(NO)_2BF_4$ (4 mmol) was added 2-methylpropene (25 mL, ca. 60-fold excess) that had been previously condensed and maintained at −78 °C. The resulting reaction mixture was stirred for 2.5 h while being maintained at −10 °C with no apparent color change occurring. The final green solution was filtered through alumina (3 × 4 cm, Woelm neutral, activity 1) supported on a medium-porosity frit to remove the cationic organometallic complex. The clear, colorless filtrate was concentrated under reduced pressure to 20 mL, and a gas chromatographic analysis of this solution showed it to contain four organic products. Analyses by GC–MS and ^1H NMR spectroscopy of the fractions separated by preparatory GC methods revealed these products to be as follows.

(1) 2,4,4,6,6-Pentamethyl-2-heptene (28% of product mixture):[14] ^1H NMR ($CDCl_3$) δ 5.16 (m, 1 H, =C*H*), 1.68 (m, 6 H, 2 CH_3), 1.43 (s, 2 H, CH_2), 1.13 (s, 6 H, 2 CH_3), 0.93 (s, 9 H, 3 CH_3); low-resolution mass spectrum (probe temperature 80 °C) *m/z* 168 (P^+).

(2) 2,4,4,6,6-Pentamethyl-1-heptene (27% of product mixture):[14] ^1H NMR ($CDCl_3$) δ 4.86 (m, 1 H, =CH_AH_B), 4.65 (m, 1 H, =C$H_A$$H_B$), 2.00 (s, 2 H, C$H_2$), 1.78 (s, 3 H, C$H_3$), 1.30 (s, 2 H, C$H_2$), 1.00 (s, 15 H, 5 C$H_3$); low-resolution mass spectrum (probe temperature 80 °C) *m/z* 168 (P^+).

(3) 2,4,4,6,6,8,8-Heptamethyl-2-nonene (26% of product mixture):[14] ^1H NMR ($CDCl_3$) δ 5.16 (m, 1 H, =C*H*), 1.70 (m, 6 H, 2 CH_3), 1.55 (s, 2 H, CH_2), 1.32 (s, 2 H, CH_2), 1.15 (s, 6 H, 2 CH_3), 1.03 (s, 6 H, 2 CH_3), 0.97 (s, 9 H, 3 CH_3); low-resolution mass spectrum (probe temperature 80 °C) *m/z* 224 (P^+).

(4) 2,4,4,6,6,8,8-Heptamethyl-1-nonene (19% of product mixture):[14] ^1H NMR ($CDCl_3$) δ 4.87 (m, 1 H, =CH_AH_B), 4.66 (m, 1 H, =C$H_A$$H_B$), 2.00 (s, 2 H, C$H_2$), 1.78 (s, 3 H, C$H_3$), 1.37 (s, 2 H, C$H_2$), 1.33 (s, 2 H, C$H_2$), 1.10 (s, 6 H, 2 C$H_3$), 1.03 (s, 6 H, 2 C$H_3$), 1.00 (s, 9 H, 3 C$H_3$); low-resolution mass spectrum (probe temperature 80 °C) *m/z* 224 (P^+).

Reactions of $CpM(NO)_2BF_4$ (M = Cr, Mo) with $NaBPh_4$. Both of these reactions were effected in the same manner.[10] The experimental procedure, with the chromium compound as a representative example, was as follows.

To a stirred green CH_2Cl_2 solution (40 mL) of $CpCr(NO)_2BF_4$ (2.0 mmol) was added solid $NaBPh_4$ (0.68 g, 2.0 mmol), whereupon the mixture darkened. An IR spectrum of the reaction mixture after 2 min showed a decrease in intensity of the ν_{NO}'s at 1844 and 1740 cm^{-1} due to the dinitrosyl reagent and the appearance of strong ν_{NO}'s at 1819 and 1712 cm^{-1}. These bands decreased in intensity with time as new absorptions at 1790 and 1685 cm^{-1} appeared and increased in intensity. After 1 h, the latter bands were the only features attributable to ν_{NO}'s in the IR spectrum of the reaction mixture. The final dark green mixture was then filtered through alumina (2 × 5 cm, Woelm neutral, activity 1),

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[8] (a) Chen, H. W.; Jolly, W. L. *Inorg. Chem.* **1979**, *18*, 2548. (b) Chatt, J.; Kan, C. T.; Leigh, J.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2032.

[9] Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

[10] Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785.

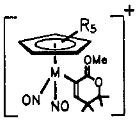
[11] Legzdins, P.; Wassink, B. *Organometallics* **1988**, *7*, 482.

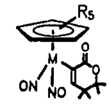
[12] Legzdins, P.; Martin, J. T.; Oxley, J. C. *Organometallics* **1985**, *4*, 1263.

[13] Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.

[14] These yields were determined by gas chromatography.

Table I. Numbering Scheme for the Cationic and Neutral Lactone Complexes





compd	no.	compd	no.
$[CpCr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$	1	$CpCr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(=O)$	7
$[Cp^*Cr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$	2	$Cp^*Cr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(=O)$	8
$[CpMo(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$	3	$CpMo(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(=O)$	9
$[Cp^*Mo(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$	4	$Cp^*Mo(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(=O)$	10
$[CpW(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$	5	$CpW(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(=O)$	11
$[Cp^*W(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$	6	$Cp^*W(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(=O)$	12

Table II. Physical Data for the Cationic Lactone Complexes 1–6

compd	color	yield, %	anal. found (calcd), % C	H	N	IR (Nujol),[a] cm^{-1}
$[CpCr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (1)	olive green	73	41.90 (41.67)	4.93 (4.86)	6.48 (6.48)	1800 (s), 1721 (s), 1665 (s), 1564 (w), 1518 (m)
$[Cp^*Cr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (2)	olive green	68	47.68 (47.81)	6.09 (6.18)	5.57 (5.58)	1763 (s), 1682 (s), 1659 (s), 1561 (w), 1512 (m)
$[CpMo(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (3)	bright green	66	38.00 (37.82)	4.35 (4.41)	5.91 (5.88)	1752 (s), 1680 (s), 1630 (s), 1564 (m), 1518 (m)
$[Cp^*Mo(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (4)	pale brown	82	44.03 (43.96)	5.63 (5.68)	4.96 (5.13)	1709 (s), 1624 (s), 1561 (m), 1520 (m)
$[CpW(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (5)	bright green	25	31.69 (31.91)	3.78 (3.72)	4.90 (4.96)	1732 (s), 1669 (s), 1618 (s), 1564 (m), 1522 (m)
$[Cp^*W(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (6)	pale green	63	37.84 (37.85)	4.93 (4.89)	4.29 (4.42)	1692 (s), 1613 (s), 1560 (m), 1522 (m)

[a] In the 1900–1500-cm^{-1} region.

Table III. ^1H NMR Chemical Shifts of the Cationic Lactone Complexes 1–6

compd	chem shift in $(CD_3)_2C=O$, δ, ppm: Cp	H	$C(CH_3)_2$	$C(CH_3)_2O$	OCH_3
$[CpCr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (1)	5.87 (s)	7.33 (s)	1.24 (s)	1.68 (s)	4.41 (s)
$[Cp^*Cr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (2)	1.87 (s)[a]	7.19 (s)	1.29 (s)	1.72 (s)	4.48 (s)
$[CpMo(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (3)	6.30 (s)	7.50 (s)	1.28 (s)	1.72 (s)	4.44 (s)
$[Cp^*Mo(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (4)	2.01 (s)[a]	7.42 (s)	1.32 (s)	1.74 (s)	4.50 (s)
$[CpW(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (5)	6.41 (s)	7.59 (s)	1.28 (s)	1.72 (s)	4.44 (s)
$[Cp^*W(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (6)	2.10 (s)[a]	7.49 (s)	1.33 (s)	1.75 (s)	4.52 (s)

[a] This is η^5-C_5Me_5.

and the alumina column was washed with CH_2Cl_2 (20 mL). The combined filtrates were taken to dryness in vacuo to obtain 0.19 g (74% yield) of $CpCr(NO)_2Ph$ as a dark green solid, which was identified by its characteristic spectroscopic properties:[15] IR (hexanes) ν_{NO} 1794 (s) and 1694 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 7.30 (m, 5 H, C_6H_5), 4.73 (s, 5 H, C_5H_5); low-resolution mass spectrum (probe temperature 120 °C) *m/z* 254 (P^+).

The known $CpMo(NO)_2Ph$ compound[15] was obtained similarly as an olive green oil in 75% yield.

Reaction of $CpMo(NO)_2BF_4$ with Phenylacetylene and 2,3-Dimethyl-2-butene. A stirred green dichloromethane solution (30 mL) of $CpMo(NO)_2BF_4$ (1.0 mmol) was cooled from room temperature to 0 °C by means of an ice bath, and a mixture of phenylacetylene (3.3 mL, 30 mmol) and 2,3-dimethyl-2-butene (3.6 mL, 30 mmol) was added to it. The reaction mixture darkened immediately upon addition of the organic reagents, and the mixture was stirred for an additional 10 min before being filtered cold through alumina in air to remove the organometallic reactant. The pale yellow filtrate was taken to dryness in vacuo to obtain 2.59 g (13.9 mmol, 13.9 turnovers based on Mo) of 3,3,4,4-tetramethyl-2-phenylcyclobutene as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 7.43–7.15 (m, 5 H, C_6H_5), 6.31 (s, 1 H, CH), 1.37 (s, 6 H, 2 CH_3), 1.18 (s, 6 H, 2 CH_3); low-resolution mass spectrum (probe temperature 170 °C) *m/z* 186 (P^+).

Reactions of $Cp'M(NO)_2BF_4$ with Methyl Propiolate and 2,3-Dimethyl-2-butene. These reactions were typically performed by using a 4- to 5-fold excess of the organic reagents.

A. M = Cr. A stirred green dichloromethane solution (40 mL) of $CpCr(NO)_2BF_4$ (3.2 mmol) was treated with a dichloromethane solution (approximately 10 mL total volume) of methyl propiolate (1.0 mL, 11 mmol) and 2,3-dimethyl-2-butene (2.0 mL, 17 mmol). The reaction mixture was then refluxed for 1 h, whereupon it darkened. After the reaction mixture had been cooled to room temperature, Et_2O (200 mL) was added to it to induce the precipitation of an olive green solid. The supernatant solution was decanted from this precipiate, which was then washed with Et_2O (40 mL) and dried at 5 × 10^{-3} mm and 20 °C for 1 h to obtain the lactone salt $[CpCr(NO)_2\overline{C=C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (complex 1) as an analytically pure, olive green solid in 73% yield based on $CpCr(NO)_2Cl$.

The analogous pentamethylcyclopentadienyl lactone salt, i.e. complex 2, was prepared in a similar manner from $Cp^*Cr(NO)_2BF_4$, the only difference being that in this case the reaction

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[15] Hoyano, J. K.; Legzdins, P.; Malito, J. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1022.

Table IV. Physical and Mass Spectral Data for the Neutral Lactone Complexes 7–12

compd	color	yield, %	anal. found (calcd), % C	H	N	MS (P^+), m/z	IR (Nujol), cm^{-1} ν_{NO}	$\nu_{C=O}$
$CpCr(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (7)	olive green	74	50.67 (50.91)	5.60 (5.45)	8.39 (8.48)	330	1786 1661	1678
$Cp^*Cr(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (8)	olive green	72	57.02 (57.00)	7.11 (7.00)	7.00 (7.00)	400	1757 1649	1684
$CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (9)	bright green	51	44.49 (44.92)	4.87 (4.81)	7.13 (7.49)	376	1737 1630	1656
$Cp^*Mo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (10)	green-brown	57	51.60 (51.35)	6.35 (6.31)	6.19 (6.13)	446	1709 1610	1680
$CpW(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (11)	bright green	71	36.60 (36.36)	4.02 (3.90)	6.02 (6.06)	462	1717 1617	1672
$Cp^*W(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (12)	bright green	63	42.95 (42.86)	5.35 (5.26)	5.19 (5.26)	532	1692 1599	1680

Table V. ^1H NMR Chemical Shifts of the Neutral Lactone Complexes 7–12

compd	chem shift in $(CD_3)_2C{=}O$, δ, ppm Cp	H	$C(CH_3)_2$	$C(CH_3)_2O$
$CpCr(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)OC}(=O)$ (7)	5.66 (s)	6.42 (s)	1.06 (s)	1.32 (s)
$Cp^*Cr(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (8)	1.81 (s)[a]	6.20 (s)	1.08 (s)	1.32 (s)
$CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (9)	6.16 (s)	6.63 (s)	1.12 (s)	1.38 (s)
$Cp^*Mo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (10)	1.94 (s)[a]	6.43 (s)	1.10 (s)	1.33 (s)
$CpW(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (11)	6.23 (s)	6.77 (s)	1.07 (s)	1.33 (s)
$Cp^*W(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (12)	2.02 (s)[a]	6.54 (s)	1.11 (s)	1.33 (s)

[a] This is η^5-C_5Me_5.

mixture had to be refluxed for 2 h in order to achieve comparable yields of the desired organometallic product.

The new lactone complexes synthesized during this work and the numbering scheme used to designate them are presented in Table I. The analytical and IR data and ^1H NMR data for the cationic complexes are collected in Tables II and III, respectively.

B. M = Mo. These reactions were performed in a manner similar to that outlined for their chromium congeners in the preceding section. In these cases, the reaction mixtures were stirred at room temperature for 45 min, and then the molybdenum lactone products were isolated in the customary manner.

C. M = W. Unlike the conversions involving chromium and molybdenum, the tungsten lactone salts could only be obtained in pure form if the reaction mixtures were filtered before being treated with Et_2O. The cyclopentadienyl case is described in the next paragraph as a representative example.

To a stirred green dichloromethane solution of $CpW(NO)_2BF_4$ (3.36 mmol in 70 mL) was added a CH_2Cl_2 solution (approximately 10 mL total volume) of methyl propiolate (1.0 mL, 11 mmol) and 2,3-dimethyl-2-butene (2.0 mL, 17 mmol). The reaction mixture immediately became very dark green, and a bright green precipitate began to deposit after 2 min. This precipitate was collected by filtration after 45 min, was washed with CH_2Cl_2 (5 mL), and was dried at 5 × 10^{-3} mm and 20 °C for 1 h to obtain 0.48 g of a bright green solid. This solid was formulated as $[CpW(NO)_2(O{=}C(OMe)C{\equiv}CH)]BF_4$ (30% yield) on the basis of its characteristic IR spectrum as a Nujol mull: ν_{NO} 1757 (s) and 1661 (vs) cm^{-1}; $\nu_{C\equiv C}$ 2122 (m) cm^{-1}; ν_{CO} 1603 (m) cm^{-1}. Unfortunately, this solid was thermally unstable, decomposing to a brown solid in less than 15 min when maintained under an atmosphere of N_2 at 20 °C. A similar decomposition occurred instantly when the solid was exposed to air. Nevertheless, treatment of the filtrate obtained during this procedure with Et_2O (120 mL) did induce the precipitation of the desired lactone salt, which was isolated in the usual manner in 25% yield.

Reaction of $[CpW(NO)_2(O{=}C(OMe)C{\equiv}CH)]BF_4$ with $P(OPh)_3$. To a stirred green slurry of $[CpW(NO)_2(O{=}C(OMe)C{\equiv}CH)]BF_4$ (0.24 g, 0.5 mmol) in dichloromethane (30 mL) at room temperature was added an excess of $P(OPh)_3$ (1.0 mL, 3.8 mmol). The reaction mixture became homogeneous in 2 min, and then Et_2O (80 mL) was added to cause the precipitation of a bright green solid. This solid was collected by filtration, washed with Et_2O (10 mL), and then dried at 5 × 10^{-3} mm and 20 °C for 1 h to obtain 0.26 g (77% yield) of $[CpW(NO)_2(P(OPh)_3)]BF_4$, which was identified by its characteristic spectroscopic properties:[10,16] IR (CH_2Cl_2) ν_{NO} 1788 (s) and 1711 (vs) cm^{-1}; ^1H NMR (acetone-d_6) δ 7.70–7.40 (m, 15 H, C_6H_5), 6.43 (d, 5 H, C_5H_5, J_{HP} = 1 Hz).

Preparation of the Neutral Lactone Complexes $Cp'M(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (7–12). These six compounds were prepared in a similar manner; the procedure employed for the synthesis of the cyclopentadienylchromium complex is outlined below as a representative example.

To a stirred green solution of $[CpCr(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ (0.910 g, 2.11 mmol) in acetone (50 mL) at room temperature was added solid NaI (0.33 g, 2.2 mmol). The reaction mixture was stirred for 45 min, whereupon it darkened, and it was then taken to dryness under reduced pressure to obtain a dark green solid. This solid was redissolved in Et_2O (70 mL), and the resulting solution was filtered through a column of alumina (2 × 3 cm, Woelm neutral, activity 1). The column was washed with THF (30 mL), and the combined filtrates were taken to dryness to yield $CpCr(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$ (7), as an analytically pure, olive green solid in 74% yield.

The physical, analytical, mass spectral, IR, and ^1H NMR data for all the neutral lactone complexes prepared during this work are presented in Tables IV and V.

Reactions of $CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(=O)$. A. With $[Me_3O]BF_4$. To a stirred green dichloromethane solution (40 mL) of the neutral molybdenum lactone compound (0.28 g, 0.75 mmol) at room temperature was added solid $[Me_3O]BF_4$ (0.11 g, 0.75 mmol). The reaction mixture was stirred for 3 h, and then Et_2O (120 mL) was added to induce the precipitation of a green solid. This solid was collected by filtration and dried in vacuo to obtain 0.20 g (56% yield) of the cationic

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[16] Stewart, R. P.; Moore, G. T. *Inorg. Chem.* **1975**, *14*, 2699.

Table VI. Crystallographic and Experimental Data for $\mathrm{CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$

formula	$C_{14}H_{18}N_2O_4Mo$	fw	399.25
cryst syst	monoclinic	space group	$P2_1/c$
a, Å	11.337 (6)	*V*	1542.5 Å^3
b, Å	12.564 (3)	*Z*	4
c, Å	11.958 (6)	μ(Mo Kα), mm^{-1}	0.8446
β, deg	115.12 (4)	D_{calcd}, g cm^{-3}	1.6116

lactone salt $\mathrm{[CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4}$, which was identified by its characteristic spectroscopic properties (vide supra).

B. With Iodine. To a stirred green Et_2O solution (70 mL) of the neutral molybdenum complex (0.83 g, 2.2 mmol) was added solid iodine (0.56 g, 2.2 mmol, of I_2). The progress of the reaction was monitored by IR spectroscopy, which revealed that the absorptions due to the organometallic lactone compound (ν_{NO} 1747 and 1655 cm^{-1}; ν_{CO} 1690 cm^{-1}) gradually diminished in intensity over a 10-h period and were ultimately replaced by absorptions at 1761 and 1676 cm^{-1} (attributable to $CpMo(NO)_2I$) and one at 1734 cm^{-1}. The ether solvent was removed from the final reaction mixture in vacuo, and the resulting black residue was extracted with hexanes (40 mL). The hexanes extract was maintained at −20 °C for 3 days to induce the crystallization of 0.17 g (27%) of the iodolactone $\mathrm{I\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$ as a pale yellow solid: ^{1}H NMR (CD_3NO_2) δ 7.35 (s, 1 H, C*H*), 1.39 (s, 6 H, 2 CH_3), 1.15 (s, 6 H, 2 CH_3); low-resolution mass spectrum (probe temperature 150 °C) *m/z* 280 (P$^+$). Anal. Calcd for $C_9H_{13}O_2I$: C, 38.57; H, 4.64. Found: C, 38.71; H, 4.80.

Decomposition of Solutions of the Neutral Tungsten Lactone Complexes in Air. Exposure of a green dichloromethane solution (30 mL) of $\mathrm{CpW(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$ (0.41 g, 0.89 mmol) to air resulted in it becoming orange after approximately 1 h and pale yellow after approximately 2 h. Drying the pale yellow solution with anhydrous Na_2SO_4 and removing the solvent from the filtrate under reduced pressure afforded 0.28 g (73% yield) of $\mathrm{CpW(O)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$ as a pale yellow solid: IR (Nujol mull) $\nu_{W{=}O}$ 953 (m) and 910 (m) cm^{-1}, ν_{CO} 1686 (s) cm^{-1}, ν_{CC} 1578 (w) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.08 (s, 1 H =C*H*), 6.66 (s, 5 H, C_5H_5), 1.38 (s, 6 H, 2 CH_3), 1.23 (s, 6 H, 2 CH_3); low-resolution mass spectrum (probe temperature 200 °C) *m/z* 434 (P$^+$).

The pentamethylcyclopentadienyl analogue $\mathrm{Cp^*W(O)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$ was obtained similarly as a pale yellow solid in 78% yield: IR (Nujol mull) $\nu_{W{=}O}$ 945 (m) and 899 (m) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.87 (s, 1 H, =C*H*), 2.18 (s, 15 H, $C_5(CH_3)_5$), 1.37 (s, 6 H, 2 CH_3), 1.18 (s, 6 H, 2 CH_3); low-resolution mass spectrum (probe temperature 200 °C) *m/z* 504 (P$^+$).

Crystal Structure Analysis of $\mathrm{CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$. A suitable green crystal of $\mathrm{CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$ was cut from a larger crystal and was sealed in a thin-walled glass capillary under dry N_2. After a preliminary photographic investigation, the crystal was transferred to an Enraf-Nonius CAD4-F diffractometer equipped with graphite-monochromated Mo Kα radiation. The crystal was cooled to 218 K by using a locally developed apparatus based on a commercial Enraf-Nonius system. The unit cell was obtained from the accurate setting angles of 25 reflections (35 < 2θ < 47°). The intensities of a unique data set were then collected by using the conventional $\theta/2\theta$ scan technique; pertinent crystallographic and experimental parameters are given in Tables VI and VII, respectively. Three standard reflections measured every 1 h showed no appreciable variation in intensity with time (<1.62%), so these standards were used to scale the data with a four-point smoothing curve. The data were corrected for Lorentz and polarization effects, and an analytical absorption correction was applied.[17]

Table VII. Data Collection and Refinement for $\mathrm{CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$

diffractometer	Enraf-Nonius CAD4-F
radiation	Mo Kα, graphite monochromator
λ of radiation, Å	0.71069
scan mode	coupled ω–2θ
scan width, deg	1.10 + 0.35 tan θ (in ω)
scan speed, deg min^{-1}	1.65–4.12 (in ω)
data collecn range	$h,k,\pm l$
2θ range, deg	0–50
size of cryst, mm	0.28 × 0.33 × 0.48
temp, K	218
transmissn factors	0.728–0.812
no. of unique rflns	2713
no. of obsd rflns[a]	2336
no. of variables	245
R_F[b]	0.021
R_{wF}[c]	0.030
goodness of fit[d]	1.637

[a] Reflections with $I > 2.5\sigma(I)$. [b] $R_F = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. [d] GOF = $[\sum w(|F_o| - |F_c|)^2/(\text{no. of degrees of freedom})]^{1/2}$.

Table VIII. Fractional Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\mathrm{CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$

atom	*x/a*	*y/b*	*z/c*	B_{eq}, Å^2
Mo	0.410134 (18)	0.055470 (15)	0.220568 (18)	1.939
N(1)	0.32962 (20)	−0.05415 (15)	0.25841 (19)	2.21
N(2)	0.37654 (19)	−0.00032 (18)	0.06930 (19)	2.66
O(1)	0.28597 (20)	−0.12588 (14)	0.29255 (19)	3.46
O(2)	0.36510 (22)	−0.04036 (18)	−0.02403 (20)	4.57
O(3)	0.31206 (17)	0.28164 (14)	0.05556 (17)	3.19
O(4)	0.13787 (16)	0.32771 (13)	0.07825 (16)	2.76
C(1)	0.59323 (31)	0.16331 (31)	0.25690 (31)	4.37
C(2)	0.52719 (31)	0.21085 (24)	0.31802 (31)	3.27
C(3)	0.53036 (28)	0.14206 (25)	0.41213 (26)	3.27
C(4)	0.60026 (29)	0.05216 (25)	0.40669 (31)	3.32
C(5)	0.63822 (29)	0.06556 (29)	0.31231 (37)	4.33
C(11)	0.23889 (23)	0.15633 (18)	0.16158 (22)	2.11
C(12)	0.13165 (24)	0.13072 (19)	0.17486 (24)	2.35
C(13)	0.01115 (23)	0.19841 (19)	0.13630 (23)	2.33
C(14)	0.05432 (24)	0.31575 (19)	0.14438 (24)	2.60
C(15)	0.23487 (23)	0.25739 (19)	0.09685 (21)	2.15
C(16)	−0.05350 (29)	0.17651 (23)	0.22337 (27)	3.06
C(17)	−0.08279 (29)	0.16642 (27)	0.00496 (27)	3.21
C(18)	0.13212 (32)	0.35341 (23)	0.27692 (27)	3.30
C(19)	−0.05741 (31)	0.39211 (25)	0.07638 (33)	3.71

Table IX. Selected Bond Lengths (Å) for $\mathrm{CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)}$

Mo–N(1)	1.813 (2)	C(1)–C(2)	1.384 (5)
Mo–N(2)	1.823 (2)	C(1)–C(5)	1.386 (6)
Mo–C(1)	2.360 (3)	C(2)–C(3)	1.407 (5)
Mo–C(2)	2.370 (3)	C(3)–C(4)	1.397 (5)
Mo–C(3)	2.374 (3)	C(4)–C(5)	1.378 (5)
Mo–C(4)	2.351 (3)	C(11)–C(12)	1.331 (3)
Mo–C(5)	2.345 (3)	C(11)–C(15)	1.478 (3)
Mo–C(11)	2.170 (2)	C(12)–C(13)	1.506 (3)
N(1)–O(1)	1.181 (3)	C(13)–C(14)	1.543 (3)
N(2)–O(2)	1.180 (3)	C(13)–C(16)	1.531 (3)
O(3)–C(15)	1.212 (3)	C(13)–C(17)	1.531 (4)
O(4)–C(14)	1.477 (3)	C(14)–C(18)	1.525 (4)
O(4)–C(15)	1.354 (3)	C(14)–C(19)	1.521 (4)

The structure was solved by conventional heavy-atom methods and refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where w was calculated from $w = [(\sigma(F_o))^2 + 0.00018F_o^{\,2}]^{-1}$. Hydrogen atoms were located in difference Fourier maps and included in the refinement with fixed isotropic temperature factors. The variables included in the refinement were a scale factor, positional parameters for all atoms, anisotropic temperature factors for the non-hydrogen atoms, and an extinction parameter.[18] The final residuals were R = 0.021 and R_w = 0.030,

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[17] Alcock, N. W. In *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1969; p 271.

Table X. Selected Bond Angles (deg) for $CpMo(NO)_2C{=}C(H)C(Me)_2C(Me)_2OC({=}O)$

N(2)–Mo–N(1)	92.3 (1)	C(11)–Mo–N(1)	92.8 (1)
C(11)–Mo–N(2)	96.9 (1)	O(1)–N(1)–Mo	174.4 (2)
O(2)–N(2)–Mo	174.3 (2)	C(5)–C(1)–C(2)	107.7 (3)
C(3)–C(2)–C(1)	108.7 (3)	C(4)–C(3)—C(2)	106.4 (3)
C(5)–C(4)–C(3)	108.7 (3)	C(4)–C(5)–C(1)	108.7 (3)
C(12)–C(11)–Mo	123.8 (2)	C(15)–C(11)–Mo	119.8 (2)
C(15)–C(11)–C(12)	116.3 (2)	C(13)–C(12)–C(11)	125.7 (2)
C(14)–C(13)–C(12)	107.3 (2)	C(16)–C(13)–C(12)	108.9 (2)
C(16)–C(13)–C(14)	111.1 (2)	C(17)–C(13)–C(12)	108.2 (2)
C(17)–C(13)–C(14)	112.3 (2)	C(17)–C(13)–C(16)	109.0 (2)
C(13)–C(14)–O(4)	108.8 (2)	C(18)–C(14)–O(4)	107.8 (2)
C(18)–C(14)–C(13)	112.9 (2)	C(19)–C(14)–O(4)	103.2 (2)
C(19)–C(14)–C(13)	113.5 (2)	C(19)–C(14)–C(18)	110.1 (2)
C(15)–O(4)–C(14)	120.5 (2)	O(4)–C(15)–O(3)	116.5 (2)
C(11)–C(15)–O(3)	124.2 (2)	C(11)–C(15)–O(4)	119.3 (2)

and the goodness of fit was 1.637. The refinement was considered complete when the ratio of all shifts to esd's was less than 0.1. The highest peak in the final difference map was 0.31 (6) e Å^{-3} and was situated 0.859 Å from C(12).

The computations were performed on a MICROVAX II computer using the NRC VAX crystal structure package[19] and the CRYSTALS suite of programs.[20] Complex neutral-atom scattering factors were taken from ref 21. Final positional and isotropic thermal parameters are presented in Table VIII, and selected bond lengths and angles are listed in Tables IX and X, respectively. Anisotropic thermal parameters for the non-hydrogen atoms (Table XI), positional and thermal parameters for the hydrogen atoms (Table XII), bond lengths and bond angles involving the hydrogen atoms (Tables XIII and XIV, respectively), and observed and calculated structure factors (Table XV) are provided as supplementary material. A thermal ellipsoid plot of the solid-state molecular structure of the compound is shown in Figure 1.[22]

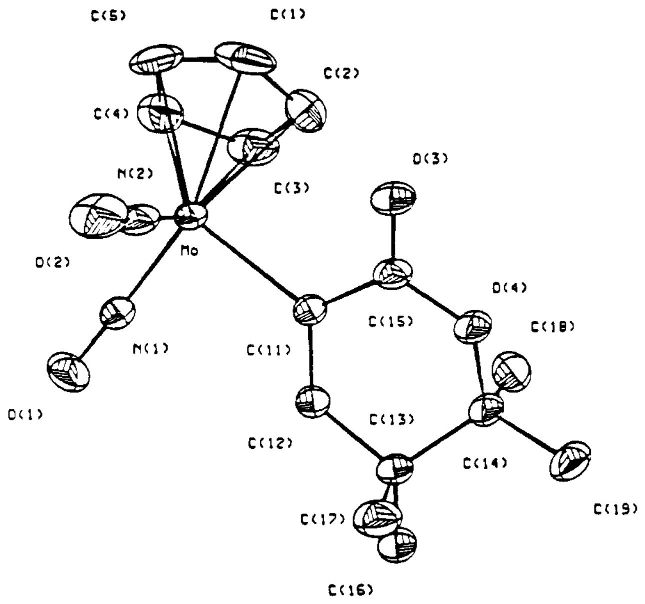


Figure 1. Solid-state molecular structure of $CpMo(NO)_2C{=}C(H)C(Me)_2C(Me)_2OC({=}O)$. Hydrogen atoms have been omitted for clarity.

Results and Discussion

Generation of Cp′M(NO)$_2$BF$_4$ (Cp′ = Cp, Cp*; M = Cr, Mo, W). All the Cp′M(NO)$_2$BF$_4$ species can be generated in situ by chloride abstraction from their Cp′M(NO)$_2$Cl precursors with an equimolar amount of AgBF$_4$ in CH$_2$Cl$_2$ (eq 1). The progress of conversions 1, which

$$Cp'M(NO)_2Cl + AgBF_4 \xrightarrow{CH_2Cl_2} Cp'M(NO)_2BF_4 + AgCl\downarrow \quad (1)$$

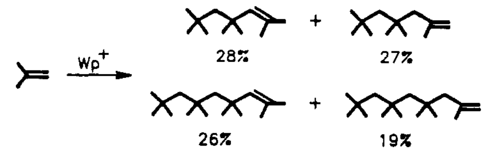
require 15–45 min to go to completion at room temperature, can be conveniently monitored by solution IR spectroscopy. The nitrosyl-stretching absorptions shift by approximately 30 cm^{-1} to higher wavenumbers as the coordinated Cl$^-$ ligand is replaced by the weakly coordinating BF$_4^-$ anion.[9,10,23] The product complexes are best formulated as discrete ion pairs with the coordinately unsaturated, 16-electron organometallic cations possibly incorporating a molecule of solvent into each metal's coordination sphere.[10,16,24] The characteristic chemistry of the various Cp′M(NO)$_2$BF$_4$ compounds in CH$_2$Cl$_2$ is certainly dominated by their electrophilic natures, and during their reactions with various nucleophiles they behave as though they were the formally 16-electron cations Cp′M(NO)$_2^+$. For instance, all the CpM(NO)$_2$BF$_4$ complexes are sufficiently electrophilic to abstract a phenyl group from the BPh$_4^-$ anion to form the known CpM(NO)$_2$Ph compounds (eq 2). Reactions 2 probably proceed via the initial for-

$$CpM(NO)_2BF_4 + NaBPh_4 \xrightarrow{CH_2Cl_2} CpM(NO)_2Ph + NaBF_4 + BPh_3 \quad (2)$$

$$M = Cr, Mo, W^{10}$$

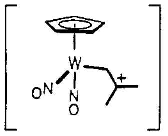
mation of CpM(NO)$_2$BPh$_4$ species, for which there exists some IR spectroscopic evidence. Thus, the chromium and molybdenum reactions proceed via intermediate species that exhibit strong ν_{NO}'s at 1819 and 1712 cm^{-1} and 1769 and 1670 cm^{-1}, respectively. These spectral features are certainly consistent with the transient presence of CpM(NO)$_2$BPh$_4$ (M = Cr, Mo) complexes. In any event, the clean production of the CpM(NO)$_2$Ph compounds via reactions 2 provides a more convenient and higher yield route to these complexes than does the original methodology, which involves treating their chloro precursors with a stoichiometric amount of Ph$_3$Al.[15]

The electrophilic nature of the formal Cp′M(NO)$_2^+$ cations is further exemplified by the reaction of the cyclopentadienyltungsten compound with 2-methylpropene, a process that results in oligomerization of the olefin as summarized in eq 3, where Wp = CpW(NO)$_2$. The oc-



(3)

currence of this oligomerization is indicative of the ability of the CpW(NO)$_2^+$ cation to generate incipient carbocations, the adduct between CpW(NO)$_2^+$ and 2-methylpropene being representable in the extreme as



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(18) Larson, A. C. In *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1969; p 291.

(19) Larson, A. C.; Lee, F. L.; Le Page, Y.; Gabe, E. J. *The NRC VAX Crystal Structure System*; Chemistry Division, National Research Council: Ottawa, Canada, 1984.

(20) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1985.

(21) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

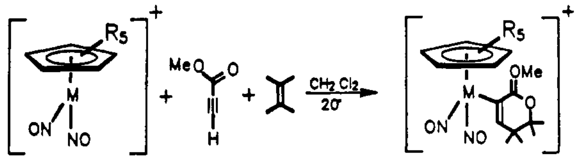
(22) Davies, E. K. *SNOOPI Plot Program*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1984.

(23) Regina, F. J.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 3803.

(24) Thus, coordinating solvents such as acetonitrile attach to the metal center and afford the isolable [Cp′M(NO)$_2$(solvent)]$^+$ cations.[7]

Such an organometallic carbocation could then be attacked by another molecule of the olefin,[25] a process that would result in the linear oligomerization observed.[28,30] Regrettably, we have not as yet succeeded in isolating a suitable crystal of a salt containing any $[Cp'M(NO)_2(olefin)]^+$ cation so that we could subject it to an X-ray crystallographic analysis in order to ascertain the solid-state molecular structure of the cation and thus gain some insight into the bonding extant in these species.

Reactions of $Cp'M(NO)_2BF_4$ with Methyl Propiolate and 2,3-Dimethyl-2-butene. When exposed to dichloromethane solutions of $Cp'M(NO)_2BF_4$, methyl propiolate and 2,3-dimethyl-2-butene condense in the metals' coordination spheres to afford the methylated lactone salts **1–6** as summarized in eq 4. The product salts resulting from reactions 4 are isolable as analytically pure, air-stable solids that are soluble in polar solvents such as nitromethane, dichloromethane, and acetone. Their solutions may also be exposed to air for at least 4 h without the occurrence of noticeable decomposition. The physical properties of these lactone-containing salts, collected in Tables II and III, are fully consistent with their monomeric formulations and with the organometallic cations possessing three-legged piano-stool molecular structures. For example, the ^1H NMR spectra of these salts are quite simple and may be assigned in a straightforward manner. An apparently inconsistent feature of these spectra is the low intensity of the singlet attributable to the protons of the cyclopentadienyl ring. This is due to the relatively long relaxation time for these protons, the measured T_1 for complex **3** being 21 s.[31] To obtain the expected signal intensities, a pulse delay of more than 50 s must thus be employed during the recording of the ^1H NMR spectra of these salts.

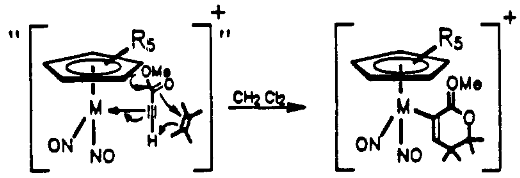


(4)

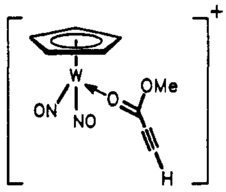
1–6

M = Cr, Mo, W; R = H, Me

Reactions 4 probably occur via initial coordination of the acetylenic ester to the metal centers in an η^2 fashion through the carbon–carbon triple bond[33] followed by nucleophilic attack on the bound ester by the free olefin in the manner shown in eq 5.[35] Consistent with this view is the fact that in the case when M = W and R = H, the progress of the general transformation (4) in dichloromethane is hampered by the precipitation of a bright green solid, which appears to be the tetrafluoroborate salt of the $CpW(NO)_2^+$ cation containing an O-bound methyl propiolate ligand:

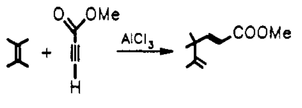


(5)

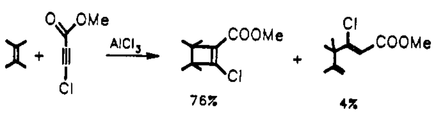


This thermally unstable salt is fairly insoluble in dichloromethane, and it decomposes in the solvents in which it does dissolve. Consequently, consistent ^1H NMR data for this species have not as yet been obtained. Nevertheless, its IR spectrum as a Nujol mull does exhibit absorptions attributable to the methyl propiolate ligand. Thus, as expected, ν_{CO} of the ester diminishes in energy (by 118 cm^{-1} from 1721 to 1603 cm^{-1}) upon coordination to the metal center whereas $\nu_{C\equiv C}$ remains relatively constant (from 2128 cm^{-1} free to 2122 cm^{-1} bound).[36] The ester is not bound very tightly to the metal center, however, and it is easily displaced by the stronger Lewis base $P(OPh)_3$ to form the known complex $[CpW(NO)_2(P(OPh)_3)]BF_4$[10,16] in high yield.

It thus appears that in the cyclopentadienyltungsten case there are two competing reaction pathways operative when $CpW(NO)_2BF_4$ is treated with methyl propiolate and 2,3-dimethyl-2-butene. One leads to the lactone-containing salt as depicted in eq 4, and the other simply involves the filling of the coordination site on the metal by the ester coordinating through one of the lone pairs of electrons on its carbonyl oxygen atom. The latter pathway leads to the insoluble $[CpW(NO)_2(O{=}C(OMe)C{\equiv}CH)]BF_4$ complex, which, in turn, reduces the amount of the $CpW(NO)_2^+$ cation available for effecting transformation 4 and accounts for the relatively low isolated yield (25%) of the desired lactone-containing salt (i.e., complex **5**) in this instance. The attachment of the $CpW(NO)_2^+$ cation to the carbonyl oxygen of the acetylenic ester is reminiscent of the $AlCl_3$-catalyzed condensation reactions presented in eq 6 and 7, which are believed to involve coordination of the



(6)



(7)

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[25] It has been calculated that it is indeed such distorted modes of linkage that render bound olefins susceptible to nucleophilic attack.[26] There has also been some experimental evidence that molecular distortions in metal–olefin complexes of the form defined by the theoretical calculations may play a significant role in determining their reactivity with nucleophiles.[27]

[26] Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148.

[27] Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.

[28] These oligomers are identifiable by their characteristic ^1H NMR spectral data,[29] which are presented in the Experimental Section.

[29] Francis, S. A.; Archer, E. D. *Anal. Chem.* **1963**, *35*, 1363.

[30] Procedures for the isolation and characterization of complex hydrocarbon mixtures have been outlined: (a) Stehling, F. C.; Bartz, K. W. *Anal. Chem.* **1966**, *38*, 1467. (b) Archer, E. D.; Shively, J. H.; Francis, S. A. *Anal. Chem.* **1963**, *35*, 1369 and references therein.

[31] It is not uncommon to find such long relaxation times for the cyclopentadienyl protons in CpM(NO)-containing complexes (M = Mo, W).[12,32]

[32] Hunter, A. D.; Legzdins, P. *Organometallics* **1986**, *5*, 1001.

[33] Isolable alkyne adducts of these dinitrosyl cations remain unknown. The only related species of this type presently known are $[CpM(NO)_2(\eta^2\text{-cyclooctene})]^+$ (M = Mo,[34] W[10]).

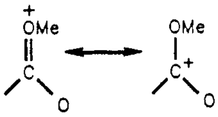
[34] Hames, B. W.; Legzdins, P. *Organometallics* **1982**, *1*, 116.

[35] In contrast, some acetylenes without heteroatom substituents (e.g. phenylacetylene) simply undergo catalyzed [2 + 2] cycloaddition reactions with 2,3-dimethyl-2-butene in the presence of $CpM(NO)_2BF_4$ (e.g. M = Mo) to produce the corresponding cyclobutene (e.g. 3,3,4,4-tetramethyl-2-phenylcyclobutene, as outlined in the Experimental Section).

[36] For a general discussion of the bonding of aldehyde and ketone ligands in organometallic complexes, see: Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298.

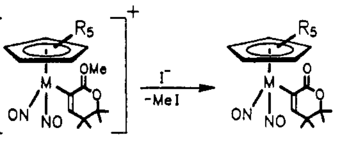
$AlCl_3$ as a Lewis acid to the carbonyl oxygen of the acetylenic esters in the transition states of the transformations.[37-40] However, since no such [2 + 2] cycloaddition or diene products are formed during any of the reactions of $Cp'M(NO)_2^+$ with methyl propiolate and 2,3-dimethyl-2-butene, it appears that entirely different transition states (e.g. those depicted in eq 5) are involved during these latter conversions that lead to the cationic lactone-containing salts.

Condensation reactions 4 bear some resemblance to the condensations of alkanoic esters with olefins that are catalyzed by the related $CpFe(CO)_2^+$ cation.[41] However, reactions 4 afford higher yields of the desired lactone products, and significant differences are that, unlike the iron case, there is no evidence for the formation of any five-membered-ring lactone products or organic byproducts during transformations 4. These facts are indicative of the greater electrophilicity of the nitrosyl cations being manifested in both a more selective and a cleaner overall conversion. Furthermore, even though the positive charge is represented as being delocalized over the entire organometallic cation in eq 4, it is probable that it is primarily centered on the methoxy group of the lactone ligand. Such a localization would permit the resonance stabilization of the cation in a manner previously invoked for organic alkoxymethyl cations.[42]



If the positive charge is situated primarily on the lactone functionality as shown above, then treatment of the cationic complex with soft nucleophiles should result in the discharge of the cation by an O-dealkylation process.[43] Indeed, as described in the next section, that is exactly what occurs.

Preparation of the Neutral Lactone Complexes $Cp'M(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)$ (7-12). The organometallic complex 7-12 are obtainable by treatment of acetone solutions of their precursor cationic lactone salts (i.e. 1-6) with equimolar amounts of sodium iodide as summarized in eq 8. The organometallic product complexes of these transformations are green to brown solids that are readily soluble in organic solvents. As pure solids, they are stable in air for short periods of time but are best stored under dinitrogen. The physical, analytical, mass spectral, and IR data for these six complexes are collected in Table IV, and their ^1H NMR data are presented in Table V. All these data are consistent with the neutral lactone complexes possessing monomeric, three-legged piano-stool molecular structures. Thus, the low-resolution mass spectra of all the neutral complexes exhibit signals due to the parent ions as their highest m/z peaks. Furthermore, a comparison of the ^1H NMR data presented in Tables III and V reveals that only small changes (i.e. 0.1-0.4 ppm) in the chemical shifts of the proton resonances occur in going from the cationic to the neutral lactone complexes. The notable absence of peaks around 4 ppm in the ^1H NMR spectra of the complexes 7-12 is a reflection of the success of the O-dealkylation reactions 8. The largest shift of approximately 1 ppm upfield is displayed by the signals attributable to the olefinic protons, and as will be shown in the next section, the presence of greater conjugation in the α,β-unsaturated group of the lactone ligand may well be responsible for this. In other words, the presence or absence of the Me^+ groups on the carbonyl portion of the lactone ligand most influences the position of the olefinic proton resonance. The intramolecular dimensions of a representative neutral lactone complex have been established by a single-crystal X-ray crystallographic analysis of complex 9.



(8)

M = Cr, Mo, W; R = H, Me

Crystal and Molecular Structures of $CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)$ (9). The crystal structure of $CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)$ consists of the packing of discrete monomeric molecular units separated by normal intermolecular contact distances. Each molecular unit, a view of which is shown in Figure 1, involves the familiar three-legged piano-stool geometry about the metal center. Selected bond lengths and angles extant in the structure are presented in Tables IX and X, respectively. Although no other neutral compounds containing the $CpMo(NO)_2$ fragment have as yet been structurally characterized, the intramolecular dimensions of this unit in the neutral lactone complex appear to be normal when compared to those previously determined for the congeneric $CpM(NO)_2Cl$ (M = Cr, W) compounds.[44] For instance, the N(2)-Mo-N(1) bond angle of 92.3 (1)° is close to that exhibited by the $CpM(NO)_2Cl$ complexes, i.e. 93.9° for M = Cr and 92.0° for M = W.[44] In addition, the O(1)-N(1)-Mo and O(2)-N(2)-Mo angles of 174.4 (2) and 174.3 (2)° indicate that the nitrosyl ligands in the lactone complex are essentially linear. Interestingly, the O(4)-C(15) bond is short (1.354 (3) Å) in comparison to the O(4)-C(14) bond (1.477 (3) Å), a relative shortness that is indicative of the former linkage possessing some double-bond character, i.e. possibly some participation of the resonance form $-C(O^-){=}O^+{-}C$ in this portion of the lactone ring.[45] Furthermore, the C(11)-C(15) bond distance of 1.478 (3) Å is shorter than that expected for an unconjugated C-C bond of this type (i.e. 1.497 Å) but is similar to that expected for the conjugated α,β-unsaturated ketone form (i.e. 1.47 Å).[46] These features suggest some delocalization of electron density over the entire C(12)-O(4) fragment. In any event, the neutral lactone complex can thus be viewed as an elaborate $CpMo(NO)_2R$ complex, the simpler hydrocarbyl analogues of which have been known for some time.[15]

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[37] Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.

[38] Snider, B. B.; Roush, D. M.; Rodini, D. J.; Gonzalez, D.; Spindell, D. *J. Org. Chem.* **1980**, *45*, 2773.

[39] Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283.

[40] Snider, B. B.; Roush, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1906.

[41] (a) Rosenblum, M.; Scheck, D. *Organometallics* **1982**, *1*, 397. (b) Samuels, S. B.; Berryhill, S. R.; Rosenblum, M. *J. Organomet. Chem.* **1979**, *166*, C9.

[42] Ramsey, B. G.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 3058.

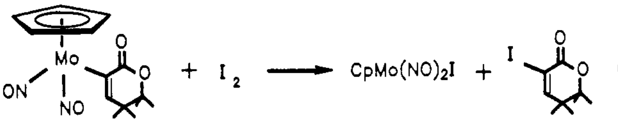
[43] For other examples of O-dealkylation in organometallic chemistry, see: (a) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.

[44] Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 795.

[45] Similar situations have been well documented for various structurally characterized carboxylic esters: Schweizer, W. B.; Dunitz, J. D. *Helv. Chim. Acta* **1982**, *65*, 1547.

[46] Allen, F. H. *Acta Crystallogr., Sect. B* **1981**, *B37*, 890.

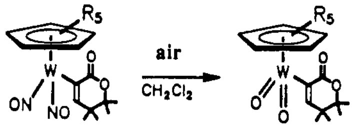
Some Derivative Chemistry of $CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)$. Methylation of the neutral lactone complex in dichloromethane with $[Me_3O]BF_4$ regenerates the precursor salt $[CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}(OMe)]BF_4$ as the only isolable organometallic product in moderate yields. This transformation, the reverse of that presented in eq 8, is consistent with the view that both the cationic and neutral lactone complexes possess similar molecular structures. Furthermore, it can be noted that the σ-bound lactone ligand may be conveniently removed from the molybdenum's coordination sphere in the neutral complex simply by treating it with molecular iodine, a reagent conventionally employed for such purposes:[41] The overall result of reactions 4, 8, and



(9)

9 is thus the stoichiometric assembly in a regiospecific manner of the iodolactone from its components, namely methyl propiolate, 2,3-dimethyl-2-butene, and iodine.

Decomposition of Solutions of the Neutral Tungsten Lactone Complexes in Air. When exposed to air at room temperature, the initially green dichloromethane solutions of the neutral tungsten lactone complexes **11** and **12** first become orange and then yellow over the course of several hours (2 h for **11** and 6 h for **12**) as they convert cleanly to the corresponding dioxo lactone species[47] (eq 10).



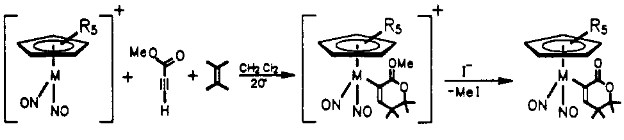
(10)

R = H, Me

The dioxo products are isolable in high yields (70–80%) and have been characterized fully by conventional spectroscopic techniques. Their IR spectra as Nujol mulls are devoid of nitrosyl absorptions, but they do contain bands at approximately 950 and 900 cm^{-1} attributable to $\nu_{W=O}$.[49] In addition, their low-resolution mass spectra exhibit the expected signals due to the parent ions as their highest m/z peaks. Finally, the ^{1}H NMR spectra of these dioxo products are qualitatively very similar to those exhibited by their dinitrosyl precursors, a feature which indicates that the Cp′W(η^1-lactone) group probably remains intact during reactions 10. The success of reactions 10 suggests that perhaps this chemistry can be extended to encompass the congeneric chromium complexes, an extension that could lead to an example of a currently unknown $CpCr(O)_2R$ (R = alkyl, aryl) type of complex. Regrettably, our initial attempts to effect this extension have not as yet been fruitful.

Epilogue

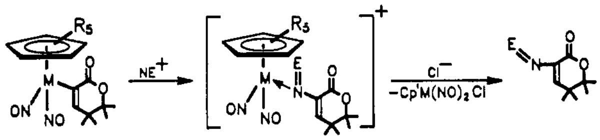
This work has shown that the 16-electron organometallic cations $Cp'M(NO)_2^+$ (M = Cr, Mo, W) are potent electrophiles which cleanly effect the regiospecific condensation of methyl propiolate and 2,3-dimethyl-2-butene to form the cationic lactone complexes **1**–**6**, which are isolable as their tetrafluoroborate salts. These salts can be converted in turn to the neutral lactone compounds **7**–**12** by treatment with NaI in acetone, as summarized in eq 11, where R = H, Me. Furthermore, the tungsten complexes **11** and **12** convert to their dioxo derivatives $Cp'W(O)_2(\eta^1\text{-lactone})$ upon exposure of their dichloromethane solutions to air.



1–6 **7–12**

(11)

We have previously shown that the electrophiles NE$^+$ (E = O, $p\text{-}O_2NC_6H_4N$, S) undergo unprecedented insertions into the Cr–C σ bonds of various $CpCr(NO)_2R$ compounds (R = Me, CH_2SiMe_3, Ph) to afford $[CpCr(NO)_2(N(E)R)]^+$ cationic complexes in good yields.[50] Consequently, the question then arises as to whether the sequential transformations outlined in eq 12 may be cleanly



(12)

M = Cr, Mo, W; E = O, S, NAr; R = H, Me

effected. If they can, this synthetic route would then lead to the formation of new types of α-substituted lactones that, to the best of our knowledge, do not have any literature precedents. Preliminary attempts to perform reactions 12 suggest that these transformations are indeed feasible,[51] although the optimum experimental conditions for isolation of the desired products in pure form have yet to be established. It is also possible that the NE$^+$ electrophiles may not only attack the metal–carbon σ bonds of the organometallic reactants but may also be involved in electrophilic attack at the carbonyl oxygen atoms of the lactone ligands, a process that would afford the $(C{=}ONE)^+$ analogues of the cationic lactone salts **1**–**6**. Whatever the case may be, it is clear that the reactions outlined in eq 12 constitute a promising area of research that should lead to new transition-metal-mediated methods for the production of fine organic chemicals.

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Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms, positional and thermal parameters for the hydrogen atoms, and bond lengths and bond angles involving the hydrogen atoms of $CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)$ (5 pages); a listing of observed and calculated structure factors for $CpMo(NO)_2\overline{C{=}C(H)C(Me)_2C(Me)_2OC}({=}O)$ (19 pages). Ordering information is given on any current masthead page.

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(47) The $CpW(NO)_2Fc$ compound (Fc = ferrocenyl) has been reported to undergo a similar conversion to $CpW(O)_2Fc$.[48]

(48) Herberhold, M.; Kneisel, H.; Haumaier, L.; Gieren, A.; Ruiz-Pérez, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 1431.

(49) Legzdins, P.; Phillips, E. C.; Sánchez, L. *Organometallics* **1989**, *8*, 940.

(50) Legzdins, P.; Richter-Addo, G. B.; Wassink, B.; Einstein, F. W. B.; Jones, R. H.; Willis, A. C. *J. Am. Chem. Soc.* **1989**, *111*, 2097.

(51) Richter-Addo, G. B.; Legzdins, P. Unpublished observations.