centered with the use of the Enraf-Nonius program.[40] These reflections were then used to obtain an orientation matrix for data collection and suggested a monoclinic cell of dimensions a = 8.579 (1) Å, b = 14.612 (3) Å, c = 11.771 (3) Å, and β = 99.26 (1)° with V = 1456.4 (9) Å^3. The observed volume is consistent with that expected for Z = 4 and a d(calcd) = 1.775 g/cm^3. The observed systematic extinctions ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) uniquely defined the space group $P2_1/c$ (No. 14, C_{2h}^5).

A graphite single-crystal incident beam monochromator was used for data collection with Mo Kα radiation [λ(Mo Kα_1) = 0.710 73 Å] at room temperature (takeoff angle 2.80°). A θ–2θ scan method was used with a variable scan rate ranging from 5°/min for the most intense reflections to 1°/min for the weak ones. The angular scan width (ω) was variable and amounted to (1.0 + 0.347 tan θ)° both below Kα_1 and above Kα_2. Right and left backgrounds were each scanned for 25% of the total scan time. During data collection, three "standard" reflections were recorded after every 90 min of actual X-ray exposure time and were recentered automatically after every 250 reflections to monitor crystal stability and orientation. The standard reflections were used to rescale the data automatically to correct for drift during data collection (drift corrections were random and varied from 0.966 to 1.048). A total of 1916 reflections were collected for 3.0 $\leq 2\theta \leq$ 43.2°; of these 1614 had intensities with $I \geq 2\sigma(I)$ and were considered observed. No correction was made for absorption (μ = 12.95 cm^{-1} for Mo Kα).

The non-hydrogen atoms were located by direct methods using the program MULTAN78,[41] and their coordinates were determined by successive least-squares refinements. The hydrogen atoms were located and fixed at their calculated positions (C–H = 0.97 Å) and were assigned isotropic temperature parameters (B = 5.0 Å^2). Refinement of all anisotropic thermal parameters[42] of all non-hydrogen atoms and both hydrogen and non-hydrogen positional parameters using unit weights yielded a final R_1 = 0.035 and R_2 = 0.039. Here, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

In the final cycle, the maximum shift was 0.00 esd. Neutral atomic scattering factors[43] were used for all atoms and were corrected for anomalous dispersion[44] (both real and imaginary parts). The final difference map was essentially featureless with a maximum electron density of 0.15 e/Å^3 in the region of P(2).

Interatomic distances with esd's and positional and thermal parameters for the final cycle of refinement are listed in Tables III and IV, respectively. The following data are available as supplementary material: observed and calculated structure factor amplitudes (Table VI), selected weighted least-squares planes and distances of atoms from planes (Table VII), root-mean-square amplitudes of thermal vibration (Table VIII), and the stereoscopic view of the molecular structure (Figure 4).

Acknowledgment. We thank the Office of Naval Research for the support of this work. We also thank R. A. Nissan and A. Freyer for obtaining the ^{1}H NMR spectra, J. L. Desorcie for recording several of the ^{31}P NMR spectra, and P. R. Suszko for obtaining the chemical ionization mass spectra. We are grateful to the National Science Foundation for providing a Perkin-Elmer 283B infrared spectrometer.

Registry No. **2**, 21229-71-0; **3**, 86727-36-8; **4**, 81098-53-5; **5a**, 86709-54-8; **5b**, 86709-55-9; **5c**, 86709-56-0; **5d**, 86709-57-1; **6a**, 84811-29-0; **6b**, 86709-58-2; **6c**, 86711-94-6; **6d**, 86709-59-3; **6e**, 86709-60-6; **6f**, 86709-61-7; **8**, 86709-62-8; $LiBEt_3H$, 22560-16-3; $N_3P_3Cl_4(i\text{-}C_3H_7)(B^-Et_3Li^+)$, 86711-97-9; $CHBr_3$, 75-25-2; $(NPCl_2)_3$, 940-71-6; NaF, 7681-49-4; CCl_4, 56-23-5; triethylborane, 97-94-9; methyl iodide, 74-88-4; 1-hydrido-1-isopropyltetrachlorocyclotriphosphazene, 71982-86-0; isopropyl iodide, 75-30-9.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (Table VI), selected weighted least-squares planes and distances of atoms from planes (Table VII), and root-mean-square amplitudes of thermal vibration (Table VIII) and the stereoscopic view of the molecular structure (Figure 4) (11 pages). Ordering information is given on any current masthead page.

(40) All programs used in data collection, reduction, and refinement were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revised 1977.

(41) Main, P. "MULTAN78, A System of Computer Programs for the Automatic Solutions of Crystal Structures", Department of Physics, University of York: York, England, 1978; obtained from G. J. G. Williams, Brookhaven National Laboratories, Upton, N.Y.

(42) Isotropic thermal parameters are of the form $\exp[-B(\sin^2\theta)/\lambda^2]$. Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

(43) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(44) "International Tables for X-Ray Crystallography"; Knyoch Press: Birmingham, England, 1968; Vol. IV.

Functionally Substituted Derivatives of $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ (M = Cr, Mo, W) Complexes

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Received March 1, 1983

Compounds of the general type $(\eta^5\text{-}C_5H_4R)M(CO)_2NO$ have been prepared and their chemistry has been studied, where M = Cr, Mo, and W and R = CO_2CH_3, CHO, $COCH_3$, $C(CH_3)=CH_2$, and $CH[N(CH_3)_2]CH_3$. The carbomethoxy derivatives (R = CO_2CH_3) for all three metals (M = Cr, Mo, W) were obtained in yields of 12–79%. The acetyl (R = $COCH_3$) and formyl (R = CHO) derivatives were obtained only for M = Cr in yields of 79% and 56%, respectively. The isopropenyl organometallic monomers (R = $C(CH_3)=CH_2$) have been prepared for molybdenum and tungsten in good yields. Treatment of 6-(dimethylamino)fulvene with methyllithium followed by molybdenum hexacarbonyl and subsequent nitrosylation with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide gave the (dimethylamino)ethyl derivative (R = $CH[N(CH_3)_2]CH_3$; M = Mo) in 56% yield. A reaction between lithium nitrocyclopentadienide and chromium hexacarbonyl followed by acetic acid and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide gave the reduced compound $(\eta^5\text{-}C_5H_4NH_2)Cr(CO)_2NO$ in 7% yield.

Introduction

There is a small group of cyclopentadienylmetal compounds that exhibit aromatic-type reactivity. Included within this group are ferrocene, ruthenocene, osmocene, cymantrene and its technetium and rhenium analogues, (η^5-cyclopentadienyl)tetracarbonylvanadium, (η^5-cyclo-

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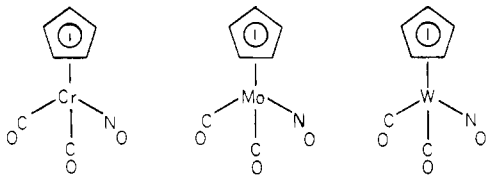
pentadienyl)dicarbonylnitrosylchromium, (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt, and (η^5-cyclopentadienyl)dicarbonylcobalt.[1] This aromatic reactivity is exemplified by the ability of these compounds to undergo electrophilic aromatic substitution reactions such as Friedel–Crafts acylation.

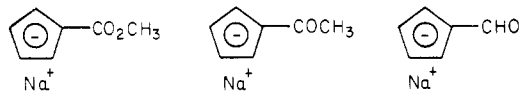
(η^5-Cyclopentadienyl)dicarbonylnitrosylmetal complexes of chromium (**1**), molybdenum (**2**), and tungsten (**3**) were



1 **2** **3**

first reported in 1955.[2] The aromatic-type reactivity of **1**, first described by Fischer and Plesske in 1961,[3] was also the subject of a recent publication of ours.[4] The molybdenum and tungsten compounds **2** and **3**, respectively, do not exhibit aromatic-type reactivity.[5] Treatment of **2** or **3** under conditions that will acylate **1** ($AlCl_3/CH_3COCl$) leads only to the decomposition of these compounds.

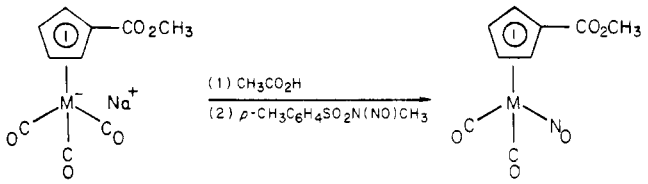
In our continuing study of the synthesis of functionally substituted cyclopentadienylmetal compounds,[6,7] we have used reagents **4–6** to prepare several substituted derivatives of **1–3**. We now wish to report details concerning the formation and chemistry of these derivatives.



4 **5** **6**

Results and Discussion

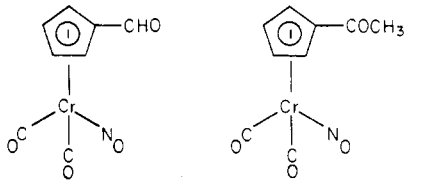
Reagents **4–6** were used as starting materials for the preparation of functionally substituted cyclopentadienyl metal complexes of chromium, molybdenum, and tungsten. Sodium carbomethoxycyclopentadienide (**4**) reacted with $Cr(CO)_6$ (DMF, reflux), $Mo(CO)_6$ (THF, reflux), and $W(CO)_6$ (DME, reflux) to give the tricarbonyl anions **7–9**.



7, M = Cr
8, M = Mo
9, M = W

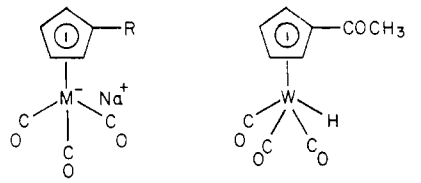
10, M = Cr
11, M = Mo
12, M = W

Treatment of anions **7–9** with acetic acid followed by subsequent nitrosylation with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide produced the respective dicarbonyl nitrosyl derivatives **10** (79%), **11** (12%), and **12** (41%). (η^5-C_5H_4CHO)$Cr(CO)_2NO$ (**13**) and (η^5-$C_5H_4COCH_3$)Cr-$(CO)_2NO$ (**14**) were prepared analogously to compound **10** in 56% and 86% yields, respectively. Compound **14** has also been obtained in lower overall yield (62%) via a Friedel–Crafts acylation of (η^5-C_5H_5)$Cr(CO)_2NO$ (**1**).[4]



13 **14**

Several attempts were made to prepare the molybdenum and tungsten analogues of **13** and **14** from anions **15–18**. When anions **15–18**[6] were treated with acetic acid followed by *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide according to literature procedures,[8–10] the expected dicarbonyl nitrosyl derivatives were not obtained. It was found that the



15, M = Mo; R = CHO
16, M = W; R = CHO
17, M = Mo; R = $COCH_3$
18, M = W; R = $COCH_3$

19

intermediate tricarbonyl hydride derivatives, which resulted from the treatment of anions **15–18** with acetic acid, were not produced in appreciable yields. For example, (η^5-acetylcyclopentadienyl)tricarbonylhydridotungsten (**19**) was isolated in only 7% yield from the reaction between **18** and acetic acid in THF. Compound **19** was identified by its ^1H NMR spectrum (C_6D_6), which showed a characteristic tungsten hydride resonance at δ −6.27.

Treatment of anions directly with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, according to a method recently developed for the synthesis of the parent compounds **1–3**,[11] produced only decomposition products. It is not known at the present time why only the carbomethoxy-substituted molybdenum (**11**) and tungsten (**12**) complexes could be prepared in this series, since the formyl and acetyl analogues should have similar properties to **11** and **12**.

Sodium methylcyclopentadienide reacts with diethyl carbonate to give a mixture of (1-methyl-2-carboethoxycyclopentadienyl)sodium (**20**) and (1-methyl-3-carboethoxycyclopentadienyl)sodium (**21**). Compounds **20** and **21** were not isolated but used directly in the preparation of the chromium complexes **22** and **23** according to Scheme I. Separation of **22** and **23** could be accomplished by column chromatography on alumina.

(η^5-$C_5H_4CO_2CH_3$)$Cr(CO)_2NO$ (**10**) was saponified under mild conditions with potassium hydroxide in aqueous methanol at 25 °C to give the corresponding carboxylic acid **24** in 87% yield (70% overall yield based on $Cr(CO)_6$). Compound **24** can also be prepared from (η^5-C_5H_5)Cr-$(CO)_2NO$ (**1**), however, in only 30% overall yield based on $Cr(CO)_6$.[4] When (η^5-$C_5H_4CO_2CH_3$)$Mo(CO)_2NO$ (**11**) and (η^5-$C_5H_4CO_2CH_3$)$W(CO)_2NO$ (**12**) were treated with potassium hydroxide in methanol, dark solutions resulted. The anticipated carboxylic acids corresponding to **11** and

(1) See references in: Macomber, D. W.; Hart, W. P.; Rausch, M. D. "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R. Eds.; Academic Press: New York, 1982; Vol. 21.
(2) Fischer, E. O.; Becker, O.; Hafner, W.; Stahl, H. O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biol. Biophys.*, **1955**, *B10*, 598.
(3) Fischer, E. O.; Plesske, K. *Chem. Ber.* **1961**, *94*, 93.
(4) Rausch, M. D.; Mintz, E. A.; Macomber, D. W. *J. Org. Chem.* **1980**, *45*, 689.
(5) Mintz, E. A.; Rausch, M. D., unpublished studies.
(6) Hart, W. P. Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196.
(7) Macomber, D. W.; Hart, W. P.; Rausch, M. D.; Pittman, C. U., Jr.; Priester, R. D., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 884.
(8) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
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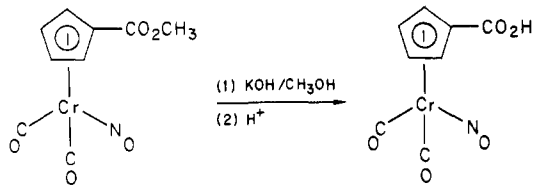
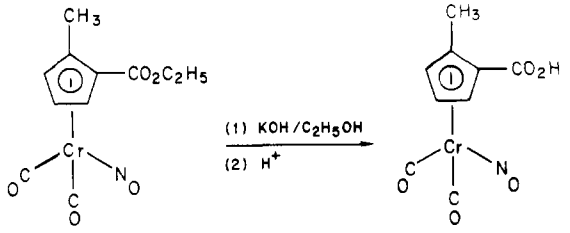
(10) Seddon, D.; Kita, W. G.; Bray, J.; McCleverty, J. A. *Inorg. Synth.* **1973**, *16*, 24.
(11) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.



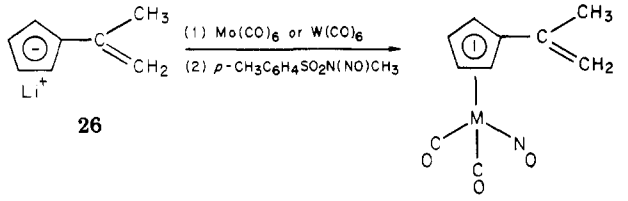
10 24

12 were not obtained upon acidification with dilute hydrochloric acid. Presumably, 11 and 12 were unstable under the basic conditions of saponification. Treatment of the chromium ester 22 under saponification conditions produced the carboxylic acid 25 in 37% yield.



22 25

We have recently found that 6,6-dimethylfulvene reacts with lithium diisopropylamide in THF to give good yields of the organolithium reagent 26.[7] Reactions on 26 with

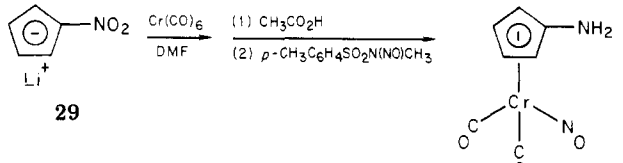


26

27, M = Mo
28, M = W

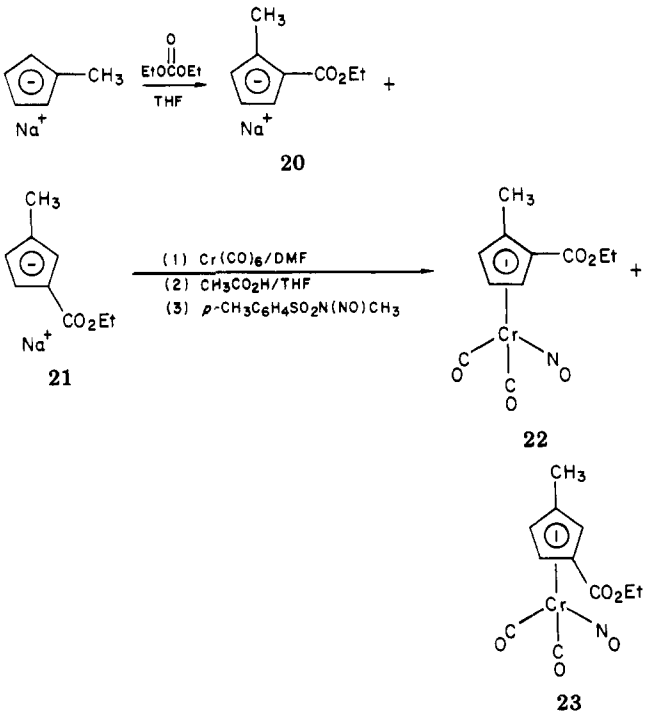
molybdenum hexacarbonyl (THF, reflux) or with tungsten hexacarbonyl (DME, reflux) followed by nitrosylation with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide afforded the organometallic monomers 27 (93%) and 28 (24%). Small amounts of $(\eta^5\text{-}C_5H_4CH(CH_3)_2)Mo(CO)_2NO$ were also formed during the preparation of 28. The chromium analogue of compounds 27 and 28 can be prepared in three steps from $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ (1) by using initially a Friedel–Crafts acylation.[4]

Lithium nitrocyclopentadienide (29) can be used to prepare $(\eta^5\text{-}C_5H_4NO_2)Rh(CO)_2$,[12] however, when used to prepare $(\eta^5\text{-}C_5H_4NO_2)Cr(CO)_2NO$, a product resulting from reduction of the nitro group was obtained. The only product isolated from this reaction was $(\eta^5\text{-}C_5H_4NH_2)Cr(CO)_2NO$ (30) in 7% yield. The reduction of aromatic nitro compounds with transition-metal carbonyls is well established,[13-15] but this is the first example of the reduction of a nitrocyclopentadienide anion.



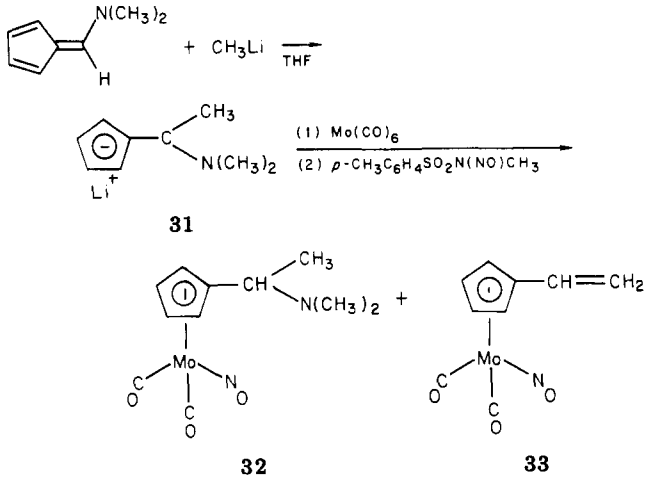
29 30

Scheme I



20 21 22 23

With methyllithium in THF as a nucleophile, lithium 1-(dimethylamino)ethylcyclopentadienide (31) was generated in situ. Molybdenum hexacarbonyl and 31 reacted in refluxing THF, and the resulting tricarbonyl anion was treated with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide to produce 32 in 56% yield. A trace of $(\eta^5\text{-}C_5H_4CH{=}CH_2)Mo(CO)_2NO$ (33)[16] was also isolated, which apparently resulted from the elimination of the elements of dimethylamine from 32.



31 32 33

Compound 32, which has an asymmetric center at the α-carbon, exhibits an A_2BB' pattern in its ^1H NMR spectrum due to the diasterotopic cyclopentadienyl protons H_2 and H_5. This effect is seen in similarly substituted cyclopentadienylmetal compounds.[4,17,18]

A similar attempt was made to generate lithium 1-(dimethylamino)methylcyclopentadienide (34) in situ. A solution of 6-(dimethylamino)fulvene was added dropwise

(12) Rausch, M. D.; Hart, W. P.; Atwood, J. L.; Zaworotko, M. J. *J. Organomet. Chem.* **1980**, *197*, 225.
(13) Alper, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 41.
(14) Alper, H.; Amaratunga, S. *Tetrahedron Lett.* **1980**, 2603.
(15) Alper, H.; Hashern, K. E. *J. Am. Chem. Soc.* **1981**, *103*, 6514.
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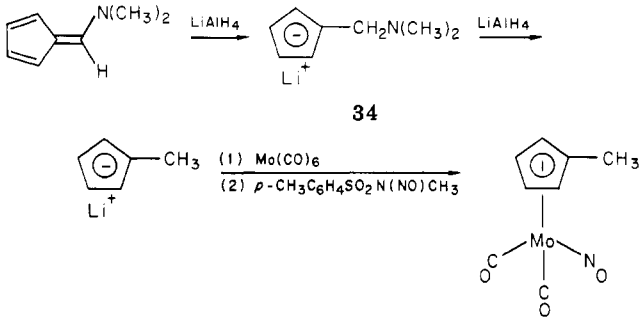
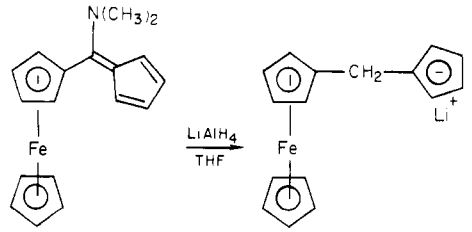
(17) Loim, A. M.; Malutschenko, L. A.; Parnes, Z. N.; Kursanov, D. N. *J. Organomet. Chem.* **1976**, *108*, 363.
(18) Loim, A. M.; Petrovskii, P. V.; Robas, V. I.; Parnes, Z. N.; Kursanov, D. N. *J. Organomet. Chem.* **1976**, *117*, 265.

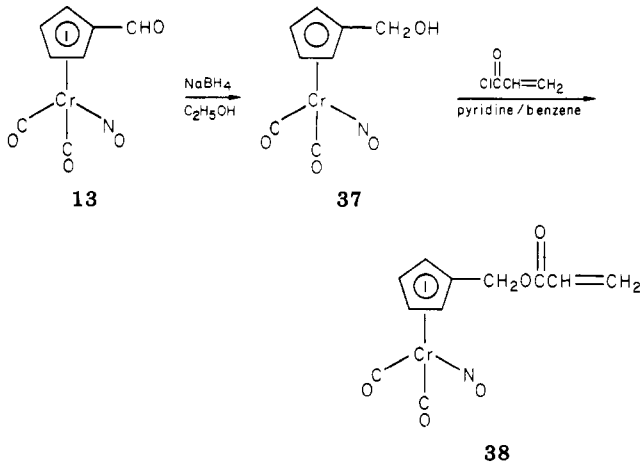
to $LiAlH_4$ in THF. This mixture was then allowed to react with molybdenum hexacarbonyl in refluxing THF and subsequently treated with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide. The only product isolated was $(\eta^5\text{-}C_5H_4CH_3)Cr(CO)_2NO$ (**35**) in 80% yield.



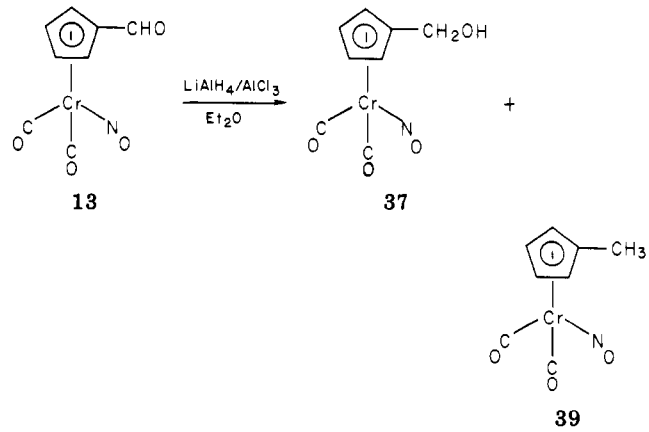
It is possible that **35** results from the reaction between molybdenum hexacarbonyl and lithium methylcyclopentadienide, which in turn is derived from the reduction of **34** with excess $LiAlH_4$. A similar reduction to produce **36** occurs during the reaction of 6-(dimethylamino)-6-ferrocenylfulvene with $LiAlH_4$.[19]



$(\eta^5\text{-}C_5H_4CHO)Cr(CO)_2NO$ (**13**) was reduced with $NaBH_4$ in ethanol to give the hydroxymethyl derivative **37** in 82% yield. Treating **37** with a mixture of acryloyl chloride and pyridine in benzene produced the acrylate monomer **38** in 56% yield. Compound **38** appears to undergo polymerization with free radical initiators similar to other acrylate monomers.[20]



When **13** was treated with 1.2-mol excess of $LiAlH_4/AlCl_3$ in ether, a mixture of $(\eta^5\text{-}C_5H_4CH_2OH)Cr(CO)_2NO$ (**37**) and $(\eta^5\text{-}C_5H_4CH_3)Cr(CO)_2NO$ (**39**) were produced in 34% and 24% yields, respectively. Compound **39** was identified by comparing it with an authentic sample of $(\eta^5\text{-}C_5H_4CH_3)Cr(CO)_2NO$, which was prepared from sodium methylcyclopentadienide in 57% yield following a literature procedure for the parent compound 1.[4] The hydrogenolysis of other ketone derivatives of **1** with $LiAlH_4/AlCl_3$ has been reported.[4]



Experimental Section

All operations were carried out under a nitrogen atmosphere using standard Schlenk or vacuum line techniques. Pentane, hexane, and dimethylformamide were dried over calcium hydride and distilled under argon. Diethyl ether was predried over sodium wire and distilled from sodium–benzophenone under argon. Tetrahydrofuran (THF) and dimethoxyethane (DME) were predried over KOH and then sodium wire and distilled under argon from sodium–benzophenone.

Column chromatography was carried out by using Fischer brand Florisil or Alfa-Ventron neutral CAMAG alumina. The Florisil and alumina were heated under vacuum (0.01 mmHg) on a rotary evaporator to remove water and oxygen. The alumina was then deactivated with 5% (by weight) argon-saturated water.

Chromium, molybdenum, and tungsten hexacarbonyls were obtained from Pressure Chemical Co. 6-(Dimethylamino)fulvene was prepared according to Hafner et al.[21] Lithium nitrocyclopentadienide (**29**) was prepared according to Hart et al.[12] Lithium isopropenylcyclopentadienide was prepared by reacting 6,6-dimethylfulvene[22,23] with lithium diisopropylamide according to the procedure described by Hart.[24] Sodium carbomethoxycyclopentadienide (**4**), sodium acetylcyclopentadienide (**5**), and sodium formylcyclopentadienide (**6**) were prepared according to literature procedures.[6,25,26]

^1H NMR spectra were recorded on a Varian A-60 spectrometer, IR spectra were recorded on either a Perkin-Elmer 237B or a Beckman IR-10 spectrometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Preparation of (η^5-Carbomethoxycyclopentadienyl)dicarbonylnitrosylchromium (10). To a solution of sodium cyclopentadienide prepared from sodium sand (0.80 g, 35.0 mmol) and cyclopentadiene (4.0 mL, 49.0 mmol) in 200 mL of DME was added dimethyl carbonate (5.90 mL, 70.0 mmol). The mixture was refluxed for 2.5 h and the solvent removed under vacuum (0.01 mmHg). DMF (150 mL) and chromium hexacarbonyl (6.00 g, 27.5 mmol) were added, and the mixture was refluxed for 5.5 h. The DMF was removed under vacuum (0.01 mmHg), and the resulting red oil was taken up in 150 mL of THF. To this was added 98% acetic acid (1.60 mL, 27.5 mmol), and the mixture was stirred for 30 min at 25 °C. *N*-methyl-*N*-nitroso-*p*-

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toluenesulfonamide (5.00 g, 23.3 mmol) was then added, and stirring was continued for 1.5 h. The THF was removed under vacuum and the resulting residue extracted with a total of 500 mL of pentane. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed under vacuum to give 5.68 g (79%) of **10** as a red liquid. An analytical sample was obtained by molecular distillation: ^{1}H NMR ($CDCl_3$) δ 3.81 (3 H, s, OCH_3), 5.14 (2 H, t, Cp $H_{3,4}$), 5.77 (2 H, t, Cp $H_{2,5}$); IR (neat) 3130 (w), 2955 (w), 2030 (s), 1955 (s), 1710 (s), 1475 (m), 1430 (w), 1365 (w), 1280 (m), 1175 (m), 1125 (m), 1030 (w), 1005 (w), 935 (w), 860 (w), 800 (w), 755 (w), 745 (w), 645 (w) cm^{-1}. Anal. Calcd for $C_9H_7CrNO_5$: C, 41.39; H, 2.70; N, 5.36. Found: C, 41.53; H, 2.83; N, 5.08.

Preparation of (η^5-Carbomethoxycyclopentadienyl)dicarbonylnitrosylmolybdenum (11). Sodium cyclopentadienide was prepared from sodium sand (0.80 g, 34.8 mmol) and cyclopentadiene (4.00 mL, 48.5 mmol) in 100 mL of DME. To this was added dimethyl carbonate (5.80 mL, 68.0 mmol), and the mixture was refluxed for 3 h. The DME was removed under vacuum, and 100 mL of THF was added. Molybdenum hexacarbonyl (9.00 g, 34.0 mmol) was added, and the mixture was refluxed for 7.5 h. To this was added 98% acetic acid (2.00 mL, 340 mmol), and the mixture was stirred for 30 min at 25 °C. *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (5.00 g, 24.0 mmol) was added with continued stirring for 2 h. The THF was removed under vacuum and the resulting dark oil extracted with 500 mL of pentane. The pentane was evaporated on Florisil under reduced pressure, and the resulting residue was added to a column of Florisil (15 × 1.5 cm). Elution of the column with pentane gave a trace orange band that was not collected. The column was eluted further with pentane/ether to give an orange band that was collected under nitrogen. The solvent was removed under vacuum to give 0.92 g (12%) of **11**. An analytical sample was obtained by sublimation at 40 °C (0.01 mmHg) as orange-yellow crystals: mp 67–69 °C; ^{1}H NMR ($CDCl_3$) δ 3.80 (3 H, s, OCH_3), 5.62 (2 H, t, Cp $H_{3,4}$), 6.23 (2 H, t, Cp $H_{2,5}$); IR (KBr pellet) 2025 (s), 1945 (s), 1720 (s), 1665 (s), 1470 (w), 1285 (m), 1135 (m) cm^{-1}. Anal. Calcd for $C_9H_7MoNO_5$: C, 35.43; H, 2.31; N, 4.59. Found: C, 35.65; H, 2.29; N, 4.53.

Preparation of (η^5-Carbomethoxycyclopentadienyl)dicarbonylnitrosyltungsten (12). Sodium cyclopentadienide was prepared from sodium sand (0.20 g, 8.7 mmol) and cyclopentadiene (2.00 mL, 24.3 mmol) in 100 mL of DME. To this was added dimethyl carbonate (1.50 mL, 17.8 mmol), and the mixture was refluxed for 2.5 h. The solution was cooled to 25 °C, tungsten hexacarbonyl (3.00 g, 8.5 mmol) was added, and the mixture was refluxed for 20 h. To this was added 98% acetic acid (0.60 mL, 10.5 mmol), and the mixture was stirred for 30 min. *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (1.10 g, 5.1 mmol) was added with continued stirring for 2 h. The DME was removed under vacuum and the resulting residue extracted with 400 mL of pentane. The pentane was evaporated on Florisil under reduced pressure and the resulting residue added to a column of Florisil (15 × 1.5 cm). Elution of the column with pentane separated a very small orange band that was not collected. The column was eluted further with pentane/ether to give another orange band that was collected under nitrogen. The solvent was removed under vacuum to produce 0.82 g (41%) of **12**. An analytical sample was obtained by recrystallization from hexane/ether as orange crystals: mp 92–94 °C; ^{1}H NMR ($CDCl_3$) δ 3.82 (3 H, s, OCH_3), 5.70 (2 H, t, Cp $H_{3,4}$), 6.26 (2 H, t, Cp $H_{2,5}$); IR (KBr pellet) 2005 (s), 1930 (s), 1715 (m), 1655 (m), 1280 (m), 1135 (w) cm^{-1}. Anal. Calcd for $C_9H_7NO_5W$: C, 27.50; H, 1.80; N, 3.56. Found: C, 27.68; H, 2.07; N, 3.64.

Preparation of (η^5-Formylcyclopentadienyl)dicarbonylnitrosylchromium (13). Sodium formylcyclopentadienide (2.90 g, 25.0 mmol) and chromium hexacarbonyl (5.50 g, 25.0 mmol) were added to a 250-mL three-neck round-bottom flask equipped with a condenser and gas inlet and outlet valves. To this was added 100 mL of DMF, and the mixture was refluxed for 3.5 h. The DMF was removed under vacuum (0.01 mmHg) to give a black oil. THF (100 mL) was then added followed by 98% acetic acid (1.48 mL, 26.0 mmol), and the mixture was stirred at 25 °C for 15 min. To this was added *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (4.28 g, 20.0 mmol), and stirring was continued for 2 h. The THF was removed under vacuum and the resulting dark oil extracted several times with pentane/ether. The combined extracts were washed well with water and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 3.25 g (56%) of **13** as a red solid. An analytical sample, mp 57–58.5 °C, was obtained by sublimation at 40 °C (0.01 mmHg): ^{1}H NMR ($CDCl_3$) δ 5.27 (2 H, t, Cp $H_{3,4}$), 5.77 (2 H, t, Cp $H_{2,5}$), 9.57 (1 H, s, CHO); IR (KBr pellet) 2020 (s), 1955 (s), 1710 (w), 1655 (s), 1450 (w), 1365 (w), 1330 (w), 1250 (w), 1160 (w), 730 (m), 680 (w) cm^{-1}. Anal. Calcd for $C_8H_5CrNO_4$: C, 41.57; H, 2.18; N, 6.06. Found: C, 41.61; H, 2.20; N, 6.04.

Preparation of (η^5-Acetylcyclopentadienyl)dicarbonylnitrosylchromium (14). Sodium acetylcyclopentadienide (0.26 g, 2.0 mmol) and chromium hexacarbonyl (0.44 g, 2.0 mmol) were added to a 100-mL three-neck round-bottom flask, followed by 40 mL of DMF. The mixture was refluxed for 3.5 h and the DMF removed under vacuum (0.01 mmHg). THF (40 mL) was added, followed by 98% acetic acid (0.13 mL, 2.2 mmol), and the mixture was stirred for 15 min at 25 °C. To this was added *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (0.41 g, 1.9 mmol), and stirring was continued for 3 h. The THF was removed under vacuum and the resulting residue extracted with a total of 250 mL of pentane. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed under vacuum to give 0.42 g (86%) of **14**. This compound exhibited identical properties (IR, NMR) as previously reported.[4]

Preparation of (η^5-Acetylcyclopentadienyl)tricarbonylhydridotungsten (19). A mixture of sodium acetylcyclopentadienide (1.70 g, 8.9 mmol) and tungsten hexacarbonyl (3.00 g, 8.5 mmol) in 100 mL of DME was refluxed for 33 h. The solution was cooled to 25 °C and filtered and the solvent removed under vacuum to give a dark oily residue. The oil was triturated with ether, yielding a yellow-brown solid that was dried at 50 °C (0.01 mmHg). The solid was dissolved in ca. 25 mL of THF and the solution cooled in ice. To this was added 98% acetic acid (0.34 mL, 6.0 mmol), and stirring was continued for 15 min at ice temperature. The solvent was removed under vacuum and the resulting residue extracted with pentane. The pentane was removed under vacuum to give 0.17 g (7%) of **19** as a pale yellow liquid: ^{1}H NMR (C_6D_6) δ −6.27 (1 H, s, WH), 2.10 (3 H, s, CH_3), 4.70 (2 H, t, Cp $H_{3,4}$), 5.32 (2 H, t, Cp $H_{2,5}$).

Preparation of (η^5-1-Methyl-2-carboethoxycyclopentadienyl)dicarbonylnitrosylchromium (22) and (η^5-1-Methyl-3-carboethoxycyclopentadienyl)dicarbonylnitrosylchromium (23). Freshly cracked methylcyclopentadiene (15.20 g, 0.19 mol) was added in four portions to 250 mL of THF containing sodium sand (3.14 g, 0.14 mol). The mixture was refluxed until all the sodium had reacted. Diethyl carbonate (33.00 mL, 0.27 mol) was added and the mixture refluxed for 6 h. The THF was then removed under vacuum (0.01 mmHg), and to the resulting residue was added 250 mL of DMF followed by chromium hexacarbonyl (24.00 g, 0.11 mol). The mixture was refluxed overnight and the DMF removed under vacuum (0.01 mmHg). THF (200 mL) was added followed by 98% acetic acid (26.00 mL, 0.44 mol) and the mixture stirred for 2 h at 25 °C. To this was added *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (30.00 g, 0.14 mol), and stirring was continued for 2 h. The THF was removed under vacuum and the resulting dark oil extracted with a total of 1 L of pentane. The combined extracts were concentrated to 400 mL under vacuum, washed with water, and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 17.10 g (53%) of **22** and **23** as a mixture of compounds. A small amount of this mixture was added to a column of alumina (30 × 2 cm). Elution of the column with hexane developed a broad red band. The first portion of this band was collected and the solvent removed under vacuum to give **22** as a red liquid: ^{1}H NMR ($CDCl_3$) δ 1.33 (3 H, t, CH_3), 2.26 (3 H, s, $CpCH_3$), 4.27 (2 H, q, CH_2), 4.97 (2 H, d, Cp $H_{4,5}$), 5.60 (1 H, t, Cp H_3). Further elution of the column with 2:1 hexane/ether brought down the remainder of the red band. The last portion of this band was collected and the solvent removed under vacuum to give **23** as a red liquid: ^{1}H NMR ($CDCl_3$) δ 1.30 (3 H, t, CH_3), 1.98 (3 H, s, $CpCH_3$), 4.24 (2 H, q, CH_2), 4.95 (1 H, t, Cp H_5), 5.67 (2 H, m, Cp $H_{2,4}$).

Preparation of (η^5-Carboxycyclopentadienyl)dicarbonylnitrosylchromium (24). Compound **10** (0.52 g, 2.0 mmol) and potassium hydroxide (0.26 g, 4.6 mmol) were dissolved

in 15 mL of methanol, and 0.40 mL of water was added. The mixture was stirred at 25 °C for 20 h and then poured into water. The solution was acidified with concentrated hydrochloric acid and cooled with ice. The resulting precipitate was collected and dried at 25 °C (0.01 mmHg) to give 0.43 g (87%) of **24**. This compound exhibited identical properties (IR, NMR) as previously reported.[4]

Preparation of (η^5-1-Methyl-2-carboxycyclopentadienyl)dicarbonylnitrosylchromium (25). Compound **22** (0.20 g, 0.7 mmol) was dissolved in 7.0 mL of absolute ethanol, and a solution of potassium hydroxide (0.09 g, 1.5 mmol) in 0.13 mL of water was added. The mixture was stirred at 25 °C for 24 h and then poured into 20 mL of water. The solution was acidified with concentrated hydrochloric acid and cooled to 0 °C. The precipitate was collected and dried at 25 °C (0.01 mmHg) to give 0.07 g (37%) of **25**. An analytical sample was obtained by repeated recrystallization from hot hexane; mp 159 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.27 (3 H, s, CH_3), 5.01 (2 H, d, Cp $H_{4,5}$), 5.68 (1 H, t, Cp H_3). Anal. Calcd for $C_9H_7CrNO_5$: C, 41.39; H, 2.70; N, 5.36. Found: C, 41.34; H, 2.88; N, 5.26.

Preparation of (η^5-Isopropenylcyclopentadienyl)dicarbonylnitrosylmolybdenum (27). In a 250-mL three-necked round-bottom flask were placed lithium isopropenylcyclopentadienide (0.56 g, 5.0 mmol) and molybdenum hexacarbonyl (1.32 g, 5.0 mmol). To this was added ca. 150 mL of THF, and the mixture was refluxed for 46 h. The solution was cooled to 25 °C, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (0.96 g, 4.5 mmol) was added, and the mixture was stirred for 1 h. The THF was removed under vacuum and the resulting residue extracted with pentane. The combined extracts were evaporated on silica gel under reduced pressure. The resulting residue was added to a column of silica gel (15 × 1.5 cm) and the column eluted with pentane. An orange band came down the column and was collected under nitrogen. The solvent was removed under vacuum to give 1.20 g (93%) of **27**. An analytical sample was obtained by several recrystallizations from pentane at −78 °C as orange needles: mp 27.5–29 °C; ^{1}H NMR ($CDCl_3$) δ 1.92 (3 H, m, $CH_3C{=}C$), 4.91 (1 H, m, vinyl), 5.28 (1 H, m, vinyl), 5.52 (2 H, t, Cp $H_{3,4}$), 5.80 (2 H, t, Cp $H_{2,5}$); IR (neat) 2020 (s), 1940 (s), 1670 (s) cm^{-1}. Anal. Calcd: C, 41.83; H, 3.16; N, 4.88. Found: C, 41.52; H, 3.09; N, 4.83.

Preparation of (η^5-Isopropenylcyclopentadienyl)dicarbonylnitrosyltungsten (28). In a 250-mL three-neck round-bottom flask were placed lithium isopropenylcyclopentadienide (0.45 g, 4.0 mmol) and tungsten hexacarbonyl (1.40 g, 4.0 mmol). To this was added ca. 150 mL of DME, and the mixture was refluxed for 6 h. The solution was cooled to 25 °C, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (0.77 g, 3.6 mmol) was added, and the mixture was stirred for 15 min. The DME was then removed under vacuum and the resulting residue extracted with pentane. The combined pentane extracts were evaporated on alumina under reduced pressure, and the resulting residue added to a column of alumina (15 × 1.5 cm). Elution of the column with pentane gave an orange band that was collected under nitrogen. The solvent was removed under vacuum to give a mixture of (η^5-isopropylcyclopentadienyl)dicarbonylnitrosyltungsten and **28**. Repeated recrystallization from pentane at −78 °C gave 0.32 g (24%) of **28** as orange crystals: mp 38–40 °C. ^{1}H NMR ($CDCl_3$) δ 1.93 (3 H, m, $CH_3C{=}C$), 4.97 (1 H, m, vinyl), 5.29 (1 H, m, vinyl), 5.59 (2 H, t, Cp $H_{3,4}$), 5.85 (2 H, Cp $H_{2,5}$); IR (neat) 2010 (s), 1925 (s), 1650 (s) cm^{-1}. Anal. Calcd: C, 32.02; H, 2.42; N, 3.74. Found: C, 31.98; H, 2.60; N, 3, 80.

Attempted Preparation of (η^5-Nitrocyclopentadienyl)dicarbonylnitrosylchromium. Preparation of (η^5-Aminocyclopentadienyl)dicarbonylnitrosylchromium (30). In a 250-mL three-neck round-bottom flask equipped with a condenser and nitrogen inlet and outlet valves was placed lithium nitrocyclopentadienide (2.34 g, 20.0 mmol) and 100 mL of DMF. The mixture was refluxed for 3 h, the solution allowed to cool to 25 °C, and the DMF removed under vacuum (0.01 mmHg). The resulting black oil was taken up in 100 mL of THF, and 98% acetic acid (1.43 ml, 25.0 mmol) was added. Stirring was continued for 1 h, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (3.43 g, 16.0 mmol) added, and the mixture stirred for 1.5 h. The THF was removed under vacuum to give a black oil. The oil was extracted several times with ether, and the combined extracts were evaporated on alumina under reduced pressure. The resulting residue was added to a column of alumina (15 × 1.5 cm). Elution of the column with hexane separated a small red band that was collected under nitrogen. Removal of the solvent under vacuum gave a trace of 1. Further elution of the column with hexane/ether gave another red band that was collected under nitrogen. The resulting product was extracted into 10% aqueous hydrochloric acid solution. The free amine was then obtained by treating the acidic extract with dilute sodium hydroxide solution and extracting this basic solution with ether. The ether extracts were washed with water and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 0.31 g (7%) of **30** as a red solid. An analytical sample was obtained by sublimation: ^{1}H NMR ($CDCl_3$) δ 3.25 (2 H, br s, NH_2), 4.60 (2 H, t, Cp $H_{3,4}$), 4.81 (2 H, t, Cp $H_{2,5}$); IR ($CDCl_3$) 3420 (m), 2020 (s), 1950 (s), 1690 (s), 1622 (m), 1520 (s), 1400 (w), 1030 (w), 820 (m), 675 (w), 630 (s) cm^{-1}. Anal. Calcd: C, 38.54; H, 2.77; N, 12.84. Found: 38.67; H, 2.98; N, 12.70.

Preparation of [η^5-(1-Dimethylamino)ethyl)cyclopentadienyl]dicarbonylnitrosylmolybdenum (32). In a 250-mL three-neck round-bottom flask equipped with a condenser and nitrogen inlet and outlet valves were placed 6-(dimethylamino)fulvene (0.50 g, 4.1 mmol) and ca. 150 mL of THF. To this was added 1.3 M methyllithium (3.30 mL, 4.3 mmol), and the mixture was refluxed for 20 h. The solution was then cooled to 25 °C, molybdenum hexacarbonyl (1.06 g, 4.0 mmol) added, and the mixture refluxed for 24 h. After the mixture was cooled to 25 °C, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (0.86 g, 4.0 mmol) was added and the mixture stirred for 1 h. The THF was removed under vacuum on Florisil and the resulting residue added to a column of Florisil (15 × 1.5 cm). Elution of the column with pentane gave an orange band that was collected under nitrogen. Removal of the solvent under vacuum gave a trace of (η^5-vinylcyclopentadienyl)dicarbonylnitrosylmolybdenum (**33**). Further elution of the column with pentane/ether produced another orange band that was collected under nitrogen. The solvent was removed under vacuum to give 0.75 g (59%) of **32**. An analytical sample was obtained by several recrystallizations from pentane at −78 °C followed by molecular distillation as an orange liquid: mp 41–43 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (3 H, d, CH_3), 2.18 [6 H, s, $N(CH_3)_2$], 3.52 (1 H, q, methine), 5.45 (2 H, t, Cp $H_{3,4}$), 5.65 (2 H, m, Cp $H_{2,5}$); IR (neat) 2010 (s), 1925 (s), 1650 (s) cm^{-1}. Anal. Calcd: C, 41.52; H, 4.43; N, 8.81. Found: C, 41.80; H, 4.40; N, 8.78.

Preparation of (η^5-Methylcyclopentadienyl)dicarbonylnitrosylmolybdenum (35). A solution of 6-(dimethylamino)fulvene (0.50 g, 4.1 mmol) in 10 mL of THF was added dropwise to an ice-cold suspension of lithium aluminum hydride (0.16 g, 4.1 mmol) in THF. The mixture was allowed to warm to 25 °C and stir for 15 h. To this was added molybdenum hexacarbonyl (1.10 g, 4.1 mmol), and the mixture was refluxed for 18 h. The solution was cooled to 25 °C, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (0.88 g, 4.1 mmol) was added, and the mixture was stirred for 1 h. The THF was removed under vacuum and the residue extracted with several portions of ether. The combined extracts were evaporated on Florisil under reduced pressure, and the resulting residue was added to a column of Florisil (15 × 1.5 cm). Elution of the column with pentane produced an orange band that was collected under nitrogen. The pentane was removed under vacuum to give 0.86 g (80%) of **35**. An analytical sample was obtained by molecular distillation as an orange liquid: ^{1}H NMR ($CDCl_3$) δ 2.18 (3 H, s, CH_3), 5.47 (4 H, s, Cp H_{2-5}); IR ($CDCl_3$) 2020 (s), 1940 (s), 1665 (s) cm^{-1}. Anal. Calcd: C, 36.80; H, 2.70; N, 5.37. Found: C, 37.02; H, 2.60; N, 5.33.

Preparation of (η^5-Hydroxymethylcyclopentadienyl)dicarbonylnitrosylchromium (37). Compound **13** (462 mg, 2.0 mmol) was dissolved in 8 mL of 95% ethanol, and sodium borohydride (38 mg, 1.0 mmol) was added. The mixture was stirred at 25 °C for 4 h, and 15 mL of 10% aqueous hydrochloric acid solution was added. The layers were separated, and the aqueous layer was extracted twice with 100-mL portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and filtered. The solvent was removed under vacuum to give 380 mg (82%) of **37** as a red liquid. An analytical sample was obtained by molecular distillation; ^{1}H NMR ($CDCl_3$) δ 2.05 (1 H, s, OH), 4.33 (2 H, s, CH_2), 4.98 (2 H, t, Cp $H_{3,4}$), 5.17 (2 H, t, Cp $H_{2,5}$);

IR (neat) 3310 (m), 2960 (w), 2880 (w), 2010 (s), 1930 (s), 1675 (s), 1410 (w), 1355 (w), 1245 (w), 1000 (m), 830 (m), 780 (m), 655 (s) cm^{-1}. Anal. Calcd: C, 41.21; H, 3.03; N, 6.01. Found: C, 41.44; H, 3.28; N, 5.85.

Preparation of (η^5-Cyclopentadienylmethyl acrylate)dicarbonylnitrosylchromium (38). Compound **37** (0.54 g, 2.3 mmol) was dissolved in 50 mL of benzene, and pyridine (0.38 mL, 4.6 mmol) was added. The mixture was cooled to 0 °C, and acryloyl chloride 0.38 mL, 4.6 mmol) was added. The mixture was then stirred for 2.5 h while warming slowly to 25 °C. The reaction mixture was poured into water and the organic layer washed three times with dilute sodium bicarbonate solution. The organic layer was then dried over anhydrous magnesium sulfate and filtered. The solvent was removed under vacuum to give 0.37 g (56%) of **38** as a red liquid. An analytical sample was obtained by molecular distillation: ^1H NMR ($CDCl_3$) δ 4.84 (2 H, s, CH_2), 5.03 (2 H, t, Cp $H_{3,4}$), 5.27 (2 H, t, Cp $H_{2,5}$), 5.76–6.46 (3 H, m, vinyl); IR (neat) 3125 (w), 2025 (s), 1950 (s), 1705 (s), 1630 (w), 1450 (w), 1400 (m), 1285 (w), 1260 (w), 1165 (s), 1055 (w), 1035 (w), 975 (m), 820 (w), 800 (m), 665 (w), 630 (s) cm^{-1}. Anal. Calcd: C, 46.00; H, 3.16; N, 4.88. Found: C, 46.24; H, 3.43; N, 4.75.

Preparation of (η^5-Methylcyclopentadienyl)dicarbonylnitrosylchromium (39). Freshly cracked methylcyclopentadiene (15.20 g, 0.19 mol) was added in four portions to 250 mL of THF containing sodium sand (3.10 g, 0.14 mol). The mixture was then refluxed until all the sodium had reacted. The THF was removed under vacuum (0.01 mmHg) followed by addition of 200 mL of DMF and chromium hexacarbonyl (24.00 g, 0.11 mol). The mixture was refluxed for 15 h and the DMF removed under vacuum (0.01 mmHg). THF (200 mL) was added followed by 98% acetic acid (13.0 mL, 0.22 mol), and the mixture was stirred for 30 min at 25 °C. To this was added slowly *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (30.00 g, 0.14 mol), and stirring was continued for 30 min. The solvent was removed under vacuum and the resulting residue extracted with a total of 1 L of pentane. The solvent was concentrated to 400 mL, washed with water, and then dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 15.2 g (57%) of **39** as a red liquid. An analytical sample was obtained by molecular distillation: ^1H NMR ($CDCl_3$) δ 1.96 (3 H, s, CH_3), 4.93 (4 H, s, Cp H_{2-5}); IR (neat) 2920 (w), 2010 (s), 1940 (s), 1685 (s), 1480 (w), 1450 (w), 1370 (w), 1170 (m), 1025 (w), 815 (m), 695 (w), 660 (m), 620 (s) cm^{-1}. Anal. Calcd: C, 44.25; H, 3.25; N, 6.45. Found: C, 44.51; H, 3.36; N, 6.40.

Reaction of (η^5-Formylcyclopentadienyl)dicarbonylnitrosylchromium (13) with Lithium Aluminum Hydride-/Aluminum Chloride. Aluminum chloride (267 mg, 2.0 mmol) was added to a stirred suspension of lithium aluminum hydride (76 mg, 2.0 mmol) in ether. After the mixture was stirred for 10 min, a solution of **13** (400 mg, 1.7 mmol) in 10 mL of ether was added dropwise. After the addition was complete, the reaction mixture was stirred for 30 min and then hydrolyzed with a solution of dilute hydrochloric acid. The ether layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed under vacuum on Florisil and the resulting residue added to a column of Florisil (15 × 1.5 cm). Elution of the column with hexane produced a red band that was collected under nitrogen. Removal of the solvent under vacuum gave 90 mg (24%) of **39**. Further elution with hexane/ether removed another red band that was collected under nitrogen. The solvent was removed under vacuum to give 160 mg (34%) of **37**.

Registry No. **10**, 73249-47-5; **11**, 73249-48-6; **12**, 73249-49-7; **13**, 79086-51-4; **14**, 64539-47-5; **19**, 86507-93-9; **22**, 86507-94-0; **23**, 86507-95-1; **24**, 72360-41-9; **25**, 86507-96-2; **26**, 77060-52-7; **27**, 80340-00-7; **28**, 80340-02-9; **29**, 75862-52-1; **30**, 86507-97-3; **32**, 86507-98-4; **33**, 80339-99-7; **35**, 86507-99-5; **37**, 86508-00-1; **38**, 86508-01-2; **39**, 86508-02-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; *p*-$CH_3C_6H_4SO_2N(NO)CH_3$, 80-11-5; MeOC(O)OMe, 616-38-6; EtOC(O)OEt, 105-58-8; CH_3CO_2H, 64-19-7; CH_3Li, 917-54-4; cyclopentadiene, 542-92-7; sodium formylcyclopentadienide, 78207-69-9; sodium acetylcyclopentadienide, 78207-70-2; methylcyclopentadiene, 26519-91-5; 6-(dimethylamino)fulvene, 696-68-4; acryloyl chloride, 814-68-6.

Homologation of Boronic Esters to α-Chloro Boronic Esters

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The homologation of boronic esters, $RBO_2C_2R'_4$ (**7**), with (dichloromethyl)lithium to form α-chloro boronic esters, R–CHCl–$BO_2C_2R'_4$ (**3**), has been found to be a highly efficient process. R may be primary, secondary, or tertiary alkyl, cycloalkyl, alkenyl, allyl, aryl, or benzyl, and functional substituents in R may include α-benzyloxy, β or remote carbalkoxy, or a remote ketal substituent. R′ was H or CH_3. The homologation failed in the presence of an α-phenylthio or an α-boronic ester substituent. The α-chloro boronic esters readily undergo nucleophilic replacement of chloride with a variety of reagents, including thiophenolate, benzyl oxide, an ester enolate, or alkyl groups from Grignard or lithium reagents. Either 100% C-alkylation or a majority of O-alkylation and Cope rearrangement could be obtained when *tert*-butyl lithioacetate reacted with pinacol 3-chloro-1-propene-3-boronate. The β-benzyloxy boronic ester (**11**) obtained by homologation of pinacol 1-(benzyloxy)pentane-1-boronate (**10**) decomposed slowly by β boron–oxygen elimination above 100 °C but was stable enough to permit replacement of the α-chlorine by methylmagnesium bromide to form **12**, which was oxidized with sodium perborate to a mixture of diastereomeric 3-(benzyloxy)-2-heptanols (**13**).

The efficient reaction of α-halo boronic esters with Grignard reagents to form carbon–carbon bonds by boron-assisted S_N2 displacement was discovered by us 20 years ago,[1] and its utility for joining sterically hindered alkyl groups has been demonstrated recently by Brown, Yamamoto, and co-workers.[2] However, the previously known routes to α-halo boronic esters[2-5] have not been

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(2) Brown H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K. *J. Org. Chem.* **1977**, *42*, 3252–3254. Brown, H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K.; Kasahara, T.; Marahashi, S.; Sonoda, A. *Ibid.* **1977**, *42*, 4088–5092.

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