nized thiol oxidation catalysts,[17,18] but solubility limitations have impeded any detailed examination. It was demonstrated that thiols are cleanly oxidized to disulfides over cobalt porphyrin polymers, a reaction that is first order in unconverted thiol and, at least over a limited range, approximately first order in cobalt complex.

Effective catalysts contained both oxidation (cobalt) and proton-acceptor sites, the carboxylate form of a cobalt-TPP-COOH resin being active and the carboxylic acid form inactive. This behavior is reminiscent of a recent report of cobalt-containing poly(4-vinylpyridine) activity,[36] wherein a similar bifunctionality was contained in the catalyst.

Effective porphyrin catalysts exhibited an apparently irreversible aging, however. Those catalyst materials which were effective in the oxidation of thiols were slowly consumed or decomposed and those ineffective were quite stable. It is suggested that the free radical processes involved in thiol oxidation lead to catalyst degradation as well and that such degradation may contribute to catalyst consumption in commercial sweetening operations.[37]

The deactivation observed in this particular application should not, however, preclude potential utility in areas such as B_{12} chemistry, coordination chemistry, and porphyrin chemistry in general.

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Arene–Metal Complexes. X. Reactivity of (η^8-Benzonorbornadiene)dicarbonylchromium in the Presence of External Ligands[1]

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Abstract: Displacement of the complexed carbon–carbon double bond of (η^8-benzonorbornadiene)dicarbonylchromium (**1**) proceeds readily only in the presence of good π-acceptor ligands. This behavior is in marked contrast to that exhibited by simple (arene)(olefin)dicarbonylchromium complexes. The stability of **1** in the presence of external ligands may be attributed to the close proximity of the olefin ligand to the metal atom, i.e., a chelation effect. The complexed carbon–carbon double bond of **1** is unreactive toward various nucleophilic reagents. The spectral properties of several (η^6-benzonorbornadiene)(ligand)dicarbonylchromium complexes (**3**) indicate that increased π-bonding to the remaining carbonyl ligands accompanies the conversion of the corresponding tricarbonyl complex to **3**. This is reflected in the behavior of complexes with structure **3** upon photolysis since in all cases the ligand is removed in preference to a carbonyl group.

An interesting new class of compounds, (alkenylarene)dicarbonylchromium complexes, has recently been formulated in our laboratory.[2] In these complexes the organic ligand contains both a benzene nucleus and a carbon–carbon double bond, and both of these groups are bonded to the metal to occupy four metal coordination sites. Since compounds of this kind might be expected to exhibit properties unlike those of simple olefin complexes,[3,4] an investigation of the reactivity of (η^8-benzonorbornadiene)dicarbonylchromium (**1**) was initiated.

Results

Complex **1**, a red crystalline solid, is readily available from photolysis (>300 nm) of (η^6-benzonorbornadiene)tri-

Table I. Reaction of (η^8-Benzonorbornadiene)-dicarbonylchromium (1) with External Ligands

Ligand	Reaction period (hr)[a]	Product
CH_3NC	0.1[b]	$C_{11}H_{10}Cr(CO)_2CNCH_3$
$(CH_3)_3NC$	0.1	$C_{11}H_{10}Cr(CO)_2CNC(CH_3)_3$
c-$C_6H_{11}NC$	0.1	$C_{11}H_{10}Cr(CO)_2CNC_6H_{11}$
$CH_3C(CH_2O)_3P$[c]	0.1	$C_{11}H_{10}Cr(CO)_2P(OCH_2)_3CCH_3$
$(CH_3O)_3As$	2.5	$C_{11}H_{10}Cr(CO)_2As(OCH_3)_3$
PF_3	9.5[d]	$C_{11}H_{10}Cr(CO)_2PF_3$
$(CH_3O)_3P$	30	$C_{11}H_{10}Cr(CO)_2P(OCH_3)_3$
$(C_6H_5)_3P$	44	$C_{11}H_{10}Cr(CO)_2P(C_6H_5)_3$
$(CH_3)_3N$	80	
Pyridine	87	
CH_3CN	84	
$C_6H_5SCH_3$	42	
Tetrahydrofuran	73	
Cyclopentene	42	
CH_3OH[e]	150	

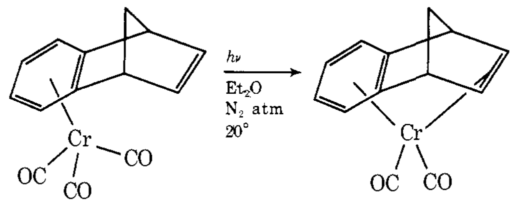
[a] The time required, under similar conditions, for 1 to be completely converted to product (as indicated by the NMR spectrum of the mixture). [b] When longer reaction times were employed tetra(methyl isocyanide)dicarbonylchromium was formed in good yields.[5] [c] 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane. [d] Trifluorophosphine at ca. 3 atm of pressure in a sealed tube. When trifluorophosphine is bubbled through a solution of 1 in benzene a much longer period is required for completion of the reaction. [e] Basic solution.

Table II. Proton NMR Data for (η^6-Benzonorbornadiene)-(ligand)dicarbonylchromium (3)[a]

Ligand	$H_{1,4}$	$H_{5,6}$	H_7	H_{Ar}	
CO	3.00	6.71	1.73	4.38	5.16
Internal olefin	2.74	2.63	0.96	4.54	5.51
CH_3NC	3.18	6.71	1.92	4.43	5.17
$(CH_3)_3CNC$	3.16	6.75	1.92	4.44	5.17
c-$C_6H_{11}NC$	3.18	6.76	1.92	4.47	5.19
$CH_3C(CH_2O)_3P$	3.18	6.83	1.89	4.62	5.28
$(CH_3O)_3As$	3.25	6.92	1.93	4.62	5.27
PF_3	2.93	6.60	1.70	4.27	5.04
$(CH_3O)_3P$	3.19	6.92	1.98	4.52	5.20
$(C_6H_5)_3P$	3.21	6.85	1.95	3.88	5.07

[a] Chemical shifts, δ; spectra were recorded with a Varian Associates A-60 instrument using 20–30% solutions in perdeuteriobenzene.

carbonylchromium (2).[2] This transformation is accompanied by a dramatic change in the NMR spectrum of the mixture since the absorption due to the olefinic protons of 2 (δ 6.71) moves far upfield (δ 2.74) when the double bond is complexed. Also readily apparent is the upfield shift (from δ 1.73 to 0.96) of the absorption for the methano bridge protons of the organic ligand when 2 is converted to 1.

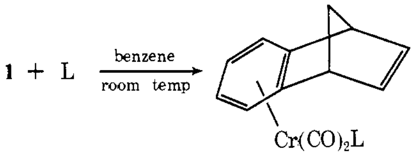


2 1

Table III. Infrared Absorption Data for (η^6-Benzonorbornadiene)-(ligand)dicarbonylchromium (3)

Ligand	Ir (cm^{-1}), CO[a]
CO	1902[b]
Internal olefin	1937, 1878
CH_3NC	1908, 1862 (2103[c])
$(CH_3)_3CNC$	1912, 1867 (2043[c])
c-$C_6H_{11}NC$	1908, 1864 (2060[c])
$CH_3C(CH_2O)_3P$	1924, 1872
$(CH_3O)_3As$	1929, 1875
PF_3	1949, 1898
$(CH_3O)_3P$	1908, 1854
$(C_6H_5)_3P$	1901, 1848

[a] Solutions in diethyl ether (1 mg/ml) and a Beckman IR-12 grating spectrophotometer were used to record the infrared spectra. [b] In carbon tetrachloride this material exhibits strong carbonyl absorptions at 1974 and 1902 cm^{-1}. [c] Absorption due to C≡N.



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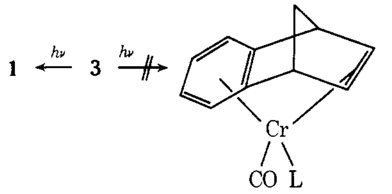
The behavior of 1 in the presence of a variety of ligands was examined. The displacement of the complexed carbon-carbon double bond of 1 (which may be conveniently monitored by NMR spectroscopy) proceeds readily in benzene at room temperature in the presence of good π-acceptor ligands (isocyanide, phosphite, arsenite, phosphine). In contrast, 1 remains unchanged when treated with several ligands which are good σ-donors but rather poor π-acceptors. These results are compiled in Table I.

In general, the products of the displacement reaction were isolated as yellow crystalline solids and characterized by physical methods. Pertinent spectral parameters for these compounds are summarized in Tables II and III.

The reactivity of 1 toward various reagents which might be expected to attack the complexed olefinic bond[6] is uniformly low.[7] Both bromine and triphenylphosphine dibromide attack the metal atom to generate free arene and ionic chromium species. Complex 1 is unaffected by treatment with hydrogen under mild conditions and remains unchanged in the presence of methyllithium or sodium methoxide-methanol.

Photolysis of compounds with structure 3 could lead to the formation of (η^8-benzonorbornadiene)(ligand)monocarbonylchromium complexes (4). However, in every case,



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photolysis of the various complexes with structure 3 regenerated 1, i.e., L rather than CO is expelled from complexes with structure 3 upon irradiation (Table IV).

Discussion

The complexed carbon-carbon double bond of complex 1 is much less reactive toward displacement by an external ligand than are nonchelated complexed carbon-carbon double bonds of simple (arene)(olefin)dicarbonylchromium compounds.[8] For example, under conditions where cyclopentene is rapidly and quantitatively displaced from (hexamethylbenzene)(cyclopentene)dicarbonylchromium by triphenylphosphine, complex 1 is only slowly (Table I) converted to 3 (L = $(C_6H_5)_3P$). A priori, displacement of the complexed carbon-carbon double bond of 1 may occur either by direct attack of external ligand at chromium or via a dissociative process in which the carbon-carbon double bond-chromium bond is ruptured prior to capture of a five-

Table IV. Photolytic Conversion of (η^6-Benzonorbornadiene)-(ligand)dicarbonylchromium complexes (3) to (η^8-Benzonorbornadiene)dicarbonylchromium (1)[a]

Ligand	Reaction period (hr)[b]	Ligand	Reaction period (hr)[b]
$CH_3C(CH_2O)_3P$	0.1	CH_3NC[c]	0.8
$(C_6H_5)_3P$	0.2	$(CH_3O)_3As$	1.25
PF_3	0.25	$(CH_3O)_3P$	1.25
$(CH_3)_3CNC$[c]	0.3	c-$C_6H_{11}NC$[c]	1.5

[a] Solutions of 3 (1 mg/ml) in diethyl ether maintained in a nitrogen atmosphere at 20° were subjected to ultraviolet radiation (>300 nm). [b] The time required for complete conversion of 3 to 1 as indicated by periodic spectroscopic analysis of the reaction mixture. [c] Substantial decomposition of complexed species occurred during the photolysis.

coordinate chromium intermediate by external ligand. Both processes have previously been implicated in the displacement, by external ligand, of bound ligands in transition metal complexes. The displacement, by isocyanide (cyclohexyl or phenyl), of halide from chloro(pentacarbonyl)tungsten anion appears to proceed via an S$_N$2 type process.[9] In contrast, for an analogous reaction in which chloro(pentacarbonyl)manganese served as substrate, the formation of a coordinatively unsaturated metal species precedes attack by external ligand.[10] Moreover, the rate-determining-step for the reaction of (η^5-cyclopentadienyl)(olefin)dicarbonylmanganese with triphenylphosphine is the initial dissociation of the olefin complex.[11] The observed order of reactivity for displacement of the complexed carbon-carbon double bond of **1** is: $CH_3C(CH_2O)_3P$, $(CH_3)_3CNC$, CH_3NC, c-$C_6H_{11}NC$ $\gg$ $(CH_3O)_3As$ $\gg$ PF_3, $(CH_3O)_3P$, $(C_6H_5)_3P$ $>\!>\!>$ $(CH_3)_3N$, pyridine, CH_3CN, $C_6H_5SCH_3$, tetrahydrofuran, cyclopentene, CH_3OH. This order clearly suggests that only good π-acceptor ligands are effective for this purpose. Indeed, more nucleophilic,[11] but σ-bonding ligands (amine, sulfides, etc.) are completely ineffective in this process. Whether the compounds of structure **3** result from direct attack of external ligands at chromium or arise from interaction of these ligands with a coordinatively unsaturated metal species is uncertain since these observations are not inconsistent with either mode of reaction. Displacement of the carbon-carbon double bond of **1** proceeds readily when this process leads to the formation of a stable complex of structure **3**, i.e. when the nucleophile present is a good π-acceptor ligand. Either **1** is unreactive in the presence of σ-bonding ligands or the products generated in these instances (**3**, L = σ-donor) are quite unstable relative to **1** and regeneration of **1** (displacement of L by the chelating carbon-carbon double bond) is facile.

Comparison of the spectral properties of compounds **3** with those of the corresponding tricarbonyl complex (**2**) indicates that substantial π-donation of electron density to the remaining carbonyl ligands occurs (40–80 cm^{-1} decrease for the infrared carbonyl absorption frequency[12]) when any ligand is substituted for a carbonyl group. Bonding of the metal to the aromatic system appears to be little affected since little change in the NMR chemical shifts for the protons of the complex's aromatic nucleus occurs when a single carbonyl group is replaced by another ligand. The increased order of the metal-carbonyl bond is also apparent from the behavior of **3** when subjected to ultraviolet irradiation since, in all cases investigated, the ligand is removed in preference to a carbonyl group. Data presented in Table III, as well as earlier results,[13] would seem to suggest that the trifluorophosphine complex (**3**, L = PF_3) would exhibit properties quite similar to those of the tricarbonyl compound (**2**). However, even in this instance, the noncarbonyl ligand is more easily lost when the complex is photolyzed.

Experimental Section

Methods and Materials. Most equipment and methods have been described previously.[14] Triphenylphosphine, trimethyl phosphite, cyclohexyl isocyanide, *tert*-butylamine, ethyl formate (distilled prior to use), dimethoxyethane, methyl phenyl sulfide, *N*-methylformamide, *o*-aminobenzoic acid, and cyclopentene were obtained from Aldrich Chemical Co. Eastman dicyclopentadiene was distilled prior to use. Quinoline[15] and *p*-toluenesulfonyl chloride[16] from J. T. Baker Chemical Co. were purified prior to use; isoamyl nitrite was used as received. Hexacarbonylchromium (Strem Chemicals, Inc.), trifluorophosphine (PCR, Inc.), and trimethylamine (Matheson Gas Products, Inc.) were used as supplied. Methyllithium was obtained as a 1.5 *M* solution in diethyl ether from Ventron-Alpha Inorganics. Solvents (dimethoxyethane, tetrahydrofuran) were distilled from lithium aluminum hydride prior to use; acetonitrile was distilled from calcium hydride. Prepurified nitrogen was used as supplied by Air Products and Chemicals, Inc. For photolyses, radiation from a 250-W General Electric sunlamp was filtered through Pyrex and a water jacket maintained at 20°.

The preparation of benzonorbornadiene and its syn tricarbonylchromium complex (**2**) and dicarbonylchromium complex (**1**) have been described previously.

Cyclopentadiene. Thermolysis of dicyclopentadiene afforded cyclopentadiene: bp 41°; NMR (CCl_4) δ 6.48 (m, 4), 2.89 (m, apparent d, 2).

***N*-*tert*-Butylformamide.** A solution of 25.75 g (0.35 mol) of *tert*-butylamine in 31.61 g (0.43 mol) of ethyl formate was stirred at reflux under nitrogen for 69 hr.[17] Excess reactants and ethanol were removed; distillation of the residue provided 21.44 g (60.2% yield) of clear, colorless *N*-*tert*-butylformamide, bp 78.5° (9.5 mm) (lit.[18] bp 202 (760 mm)): ir (CCl_4) 3453, 2984, 2895, 2772, 1708 cm^{-1}; NMR (CCl_4) δ 7.91 and 7.88 (s, 1), 7.40 (broad s, 1), 1.33 (s, 9).

***tert*-Butyl Isocyanide.** A solution of 30.63 g (0.16 mol) of *p*-toluenesulfonyl chloride in 88.85 g (0.69 mol) of quinoline was placed in a 250-ml, three-necked, round-bottomed flask fitted with a magnetic stirring bar, thermometer, pressure-equalizing dropping funnel, and a gas-exit tube connected directly to a trap maintained at −78°. The pressure inside the reaction vessel was reduced to 41 Torr, the temperature of the mixture was increased (external heating) to 80°, and 10.93 g (0.11 mol) of *N*-*tert*-butylformamide was added dropwise over a period of 0.5 hr. As it was formed, the isocyanide (bp[19] 91–92° (730 mm)) was collected in the cold trap: 6.90 g (76.8% yield); ir (CCl_4) 2997, 2953, 2139, 1377, 1242, 1222 cm^{-1}; NMR (CCl_4) δ 1.43 (1:1:1 t, J = 1.93 Hz).

Methyl isocyanide[20] was prepared by the method described above: ir (CCl_4) 2954, 2170, 937 cm^{-1}; NMR (benzene-d_6) δ 2.47 (1:1:1 t, J = 2.2 Hz).

4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane was prepared as previously described:[21] NMR (benzene-d_6, CCl_4) δ 3.52, 3.87 (d, J = 2.0 Hz, 6), 0.02, 0.72 (s, 3).

Trimethyl arsenite was prepared from trichloroarsine and sodium methoxide–methanol as described previously;[22] NMR (benzene-d_6) δ 3.52 (s).

(η^6-Benzonorbornadiene)(ligand)dicarbonylchromium Complexes (3). In general, compounds **3** were prepared by treating a benzene solution of **1** with the appropriate ligand at room temperature. The procedure described for the preparation of **3** with L = $(CH_3)_3CNC$ is illustrative of the methods generally employed.[23]

(η^6-Benzonorbornadiene)(*tert*-butyl isocyanide)dicarbonylchromium. A solution of 175.6 mg (0.70 mmol) of **1** in 1.5 ml of benzene-d_6 was treated with 255.2 mg (3.07 mmol) of *tert*-butyl isocyanide. Progress of reaction, which was complete within 5–10 min at room temperature, was monitored by periodically recording the NMR spectrum of the mixture. Solvent and excess isocyanide were removed by evaporation under a stream of nitrogen. The crude product was recrystallized from 1:1 benzene–pentane to provide 213.5 mg (91.2% yield) of **3** (L = $(CH_3)_3CNC$) as yellow needles: mp 102–103° dec; ir (Et_2O) 2043, 1912, 1867 cm^{-1}; NMR (proton, benzene-d_6) δ 6.75 (apparent t, 2), 5.17 and 4.44 (AA′**BB**′

pattern, 4), 3.16 (m, 2), 1.92 (AB pattern, 2), 1.08 s,[24] 9), (carbon, benzene-d_6) δ[26] 31.25 (methyl C), 48.79 ($C_{1,4}$), 71.93 (C_7), 86.41 ($C_{8,11}$), 89.73 ($C_{9,10}$), 120.07 ($C_{2,3}$), 142.23 ($C_{5,6}$), 238.65 (CO); mass spectrum[27] (70 eV) *m/e* (% of base) 333 (M^+, 4.5), 277[29] (5.0), 221 (4.6), 194 (17.5), 142 (100); exact mass calcd for $C_{18}H_{19}CrNO_2$, 333.0821; found, 333.0819.

(η^6-Benzonorbornadiene)(methyl isocyanide)dicarbonylchromium: yellow prisms from 1:10 ether–pentane, mp 111–112°; ir (Et_2O) 2103, 1908, 1862 cm^{-1}; NMR (benzene-d_6) δ 6.71 (m, 2), 5.17 and 4.43 (AA′BB′ pattern, 4), 3.18 (m, 2), 2.40 (s,[24] 3), 1.92 (AB pattern, 2); mass spectrum[27] (10 eV) *m/e* 291 (M^+), 235,[29] 194, 142; exact mass calcd for $C_{15}H_{13}CrNO_2$, 291.0351; found, 291.0334.

(η^6-Benzonorbornadiene)(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)dicarbonylchromium: yellow needles from 1:1 benzene–pentane (42.0% yield), mp 224–225 dec; ir (Et_2O) 1924, 1872 cm^{-1}; NMR (benzene-d_6) δ 6.83 (apparent t, 2), 5.28 and 4.62 (AA′BB′ pattern, 4), 3.59 (d, $J = 4.2$ Hz, 6), 3.14 (m, 2), 1.89 (AB pattern, $J_{AB} = 7.0$ Hz, $\Delta\nu_{AB} = 16.3$ Hz, 2), 0.01[31] (s, 3); mass spectrum[27] (10 eV) *m/e* 398 (M^+), 342,[29] 194, 142; exact mass calcd for $C_{18}H_{19}CrO_5P$, 398.0375; found, 398.0363.

(η^6-Benzonorbornadiene)(triphenylphosphine)dicarbonylchromium: fine yellow needles (45.2% yield) from 1:3 benzene–pentane, mp 169.5–170°; ir (Et_2O) 1901, 1848 cm^{-1}; NMR (benzene-d_6) 7.80–7.42 (m, 6), 7.19–6.82 (m, 11), 5.07 and 3.88 (AA′BB′ pattern, 4), 3.21 (m, 2), 1.95 (AB pattern, 2); mass spectrum[27] (70 eV) *m/e* 512[32] (M^+), 456,[29] 314.

Anal. Calcd for $C_{31}H_{25}CrO_2P$: C, 72.65; H, 4.92. Found: C, 72.82; H, 4.85.

(η^6-Benzonorbornadiene)(cyclohexyl isocyanide)dicarbonylchromium: ir (Et_2O) 2060, 1908, 1864 cm^{-1}; NMR (benzene-d_6) δ 6.76 (apparent t, 2) 5.19 and 4.47 (AA′BB′ pattern, 4), 3.18 (m, 3), 1.92 (AB pattern, $J_{AB} \sim 8$ Hz, 2), 1.72–0.59 (m, 10); mass spectrum[27] (70 eV) *m/e* (% of base) 359 (M^+), 278 (4), 222 (2), 194 (10), 142 (100); exact mass calcd for $C_{20}H_{21}CrNO_2$, 359.0977; found, 359.0982.

(η^6-Benzonorbornadiene)(trimethyl phosphite)dicarbonylchromium: ir (Et_2O) 1908, 1854 cm^{-1}; NMR (benzene-d_6) δ 6.92 (m, 2), 5.04 and 4.27 (AA′BB′ pattern, 4), 2.93 (m, 2), 1.70 (AB pattern, $J_{AB} \sim 8$ Hz, 2); mass spectrum[27] (70 eV) *m/e* (% of base) 338 (M^+, 22), 222 (11), 194 (100), 142 (100); exact mass calcd for $C_{13}H_{10}CrF_3O_2P$, 337.9776; found, 337.9771.

(η^6-Benzonorbornadiene)(trimethyl phosphite)dicarbonylchromium: ir (Et_2O) 1908, 1854 cm^{-1}; NMR (benzene-d_6) δ 6.92 (m, 2), 5.20 and 4.52 (AA′BB′ pattern, 4), 3.45 (d, $J = 11.3$ Hz, 9), 3.19 (m, 2), 1.98 (m, 2); mass spectrum[27] (70 eV) *m/e* 374 (M^+), 346, 318; exact mass calcd for $C_{16}H_{19}CrO_5P$, 374.0375; found, 374.0372.

(η^6-Benzonorbornadiene)(trimethyl arsenite)dicarbonylchromium: ir (Et_2O) 1929, 1875 cm^{-1}; NMR (benzene-d_6) δ 6.92 (m, 2), 5.27 and 4.62 (AA′BB′ pattern, 4), 3.68 (s, 9), 3.25 (m, 2), 1.93 (m, 2); exact mass calcd for $C_{16}H_{19}AsCrO_5$, 417.9853; found, 417.9873.

Photolysis of Compounds 3. The procedure described is illustrative of those generally employed for the photolysis of compounds **3**. A solution of ca. 30 mg of **3** with $L = P(OCH_3)_3$ in 50 ml of anhydrous ether maintained at 20° in a nitrogen atmosphere was subjected to ultraviolet irradiation (>300 nm). To monitor the progress of reaction, aliquots of the mixture were removed periodically and analyzed by ir spectroscopy. Over a period of 1.25 hr, the complex initially present (1908 and 1854 cm^{-1}) was smoothly converted to **1** (1937 and 1878 cm^{-1}). Removal of the solvent[23] and analysis of the residue by NMR spectroscopy confirmed the identification of product **1**.

References and Notes

(1) (a) Part IX: B. A. Howell and W. S. Trahanovsky, *J. Magn. Reson.*, in press. (b) We are grateful for a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, which provided support for this work.

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(5) The conversion of (arene)(isocyanide)dicarbonylchromium compounds to tetra(isocyanide)dicarbonylchromium complexes is currently being investigated.

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(7) Complex **1** reacts with diazomethane and benzyl azide to provide products formally derived from methylene and benzyl nitrene, respectively. Whether or not initial attack of these reagents occurs at chromium is, as yet, unclear.

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(12) The higher carbonyl stretching frequency was chosen for this comparison. The frequency at which this absorption occurs is more sensitive to changes in electron density at the chromium atom than is the lower frequency band.[8,13]

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(23) Base-washed Pyrex glassware was employed for all reactions involving metal complexes. For isolation of the complexes, solutions were concentrated by rotary evaporation of solvent at reduced pressure. The remaining solvent was then removed by evaporation of solvent under a stream of nitrogen.

(24) The singlet absorption for the isocyanide methyl protons in the spectrum of the complex is not unexpected.[25]

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(26) Spectra were recorded as previously described.[1a] The chemical shifts are accompanied by the appropriate assignment. Under the conditions employed to obtain the spectrum, absorption due to carbon atoms bound to nitrogen was not observed.

(27) In all cases, the expected isotopic cluster for chromium was observed for those fragments containing a chromium atom.[28]

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(29) The simultaneous loss, upon electron impact, of two carbonyl ligands is not uncommon for (arene)metal(carbonyl) complexes.[30]

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(31) In $CDCl_3$ this absorption appears at δ 0.73.

(32) The intensity of the molecular ion is not sufficient to permit the determination of an exact mass.