display a broad multiple between ca. τ 2.2 and 3.2 for compounds **2** to **9**. The ethyl protons of all the diazenides and hydrazides appear as a well-defined triplet and a quartet (see Table I). The dppe methylene protons of the ((ethoxycarbonyl)methyl)diazenides and -hydrazides appear as a broad multiplet at between ca. τ 6.5 and 7.5 (although **3** exhibits a triplet, see Figure 1) while **6** and **7** exhibit a broad doublet for these protons which has also been observed for other simple alkyldiazenides and -hydrazides of molybdenum.[1,3] The chemical shift of nitrogen-bound methylene protons of **2** to **7** changes with variation in the coordinated halogen atom as well as shows a difference between the corresponding diazenides and hydrazides. The resonance for the ((ethoxycarbonyl)methyl)diazenido methylene protons appears as a singlet and moves to lower field as the electronegativity of the halogen increases (see Table I). There are two effects observed when **2**, **4**, and **6** are protonated. First, the methylene protons appear as a doublet due to coupling with the nitrogen-bound proton. This would suggest that the position of the protonation is the carbon-bound nitrogen atom rather than the molybdenum-bound nitrogen atom. Second, the methylene proton resonance moves to higher field. These changes are small but reproducible.

The position of the N–H resonance is a function of the coordinated halogen atom and, more dramatically, of the alkyl group attached to the same nitrogen atom. For example, the N–H resonances shows a change of ca. 0.35 ppm upon changing from the chloro to bromo to iodo derivatives. However, there is almost a 0.9 ppm change to higher field when the (ethoxycarbonyl)methyl group of **7** is replaced by a 3-(ethoxycarbonyl)propyl group (**9**). Butyl-, cyclohexyl-, and octylhydrazido complexes of molybdenum also exhibit the N–H resonance at ca. τ 6.[1,3] Considerable variation in the N–H resonance has also been observed with changes in the counterion which can be related to the hydrogen bonding ability of the counterion.[3] This effect is eliminated in these studies since the tetrafluoroborate ion is the counterion in all four hydrazides, **3**, **5**, **7** and **9**. Addition of D_2O to deuteriochloroform solutions of the hydrazides causes the N–H resonance to disappear, and for **3**, **5**, and **7**, the methylene doublet collapses to a singlet.

The electronic absorption spectra of the (ethoxycarbonyl)methyl derivatives have been recorded in benzene (diazenides) and THF (hydrazides) solutions (see Table I) and briefly mentioned elsewhere.[15] Qualitatively, the spectra are similar to those discussed previously for the simple alkyldiazenido and -hydrazido complexes of molybdenum.[1,3,15] However, the absorption maximum at ca. 345 nm of **2**, **4** and **6** does move to higher energy as the electronegativity of the halogen atom increases: Cl (330 nm), Br (343 nm), and I (358 nm). Small changes have also been observed in this same band among the simple alkyldiazenides as the trans group has been varied among I, Br, OH, N_3, and NCS.[1,3]

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N-Benzoyl Isocyanide Group: A π-Acceptor Ligand Similar to Carbon Monoxide and a New Route[1] to Optically Active Chromium(0) Complexes

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The photochemical synthesis of $[(arene)Cr(CO)_2CN]^-$ derivatives from $(arene)Cr(CO)_3$ complexes in the presence of KCN, followed by electrophilic attack of benzoyl chloride on the cyanide ligand, affords benzoyl isocyanide complexes of the type $(arene)Cr(CO)_2(CNCOPh)$. The spectroscopic properties (^{13}C NMR and IR) of these compounds are discussed by comparision with derivatives of the type $(arene)Cr(CO)_2L$ (L = CO, CS, $CNCH_3$, $P(OPh)_3$). These results suggest that *N*-acyl isocyanides have electronic properties close to those of carbon monoxide. Specific photochemical substitution of CO by $P(OPh)_3$ in $(arene)Cr(CO)_2(CNCOPh)$ confirms the substantial strength of the Cr^0—CNCOPh bond and provides a new route to chiral complexes. Two pairs of optically active diastereoisomers, $(C_6H_5CO_2CH_3)Cr(CO)(CNCOPh)PPh_2(neomenthyl)$ and $(m\text{-}OCH_3C_6H_4CO_2CH_3)Cr(CO)(CNCOPh)P(OPh)_3$, have been prepared as synthetic applications of the latter reaction.

Introduction

Ligand substitution is probably the most important photochemical reaction of metal carbonyl derivatives. This is primarily due to the fact that photosubstitution chemistry is an essential aspect of photoinitiated transition-metal carbonyl catalysis.[2] A variety of photolabilization sites may often exist in the same complex. For example, irradiation of (arene)chromium complexes as (arene)$Cr(CO)_2L$ may involve either Cr–L cleavage[3] or dissociation of carbon monoxide.[1] We previously reported the latter type of behavior for synthesis of chiral thiocarbonyl (L = CS) complexes.[1] It was anticipated that the catalytic potential of these complexes would be particularly promising for asymmetric organic synthesis. Unfortunately, all catalytic hydrogenation attempts failed with this species.[4] This disappointing result prompted us to search for new ligands which could simultaneously provide a route to chiral complexes and facilitate catalytic activity.

Whereas alkyl and aryl isocyanides are generally believed to be stronger σ-donor than π-acceptor ligands,[5] we expected different behavior for benzoyl isocyanides ($C_6H_5C(O)NC$). The presence of the benzoyl moiety should increase the π-acceptor ability of the ligand and thus strengthen the metal–ligand bond. Accordingly, we have prepared chiral complexes of the type (η-arene)Cr(CO)(CNCOPh)$P(OPh)_3$ from (η-arene)$Cr(CO)_2$(CNCOPh). With the belief that our previous results[4,6] on the catalytic effectiveness of benzoyl isocyanide complexes were positive, the new compounds should fulfill both the synthetic and catalytic criteria. We report herein the successful synthesis and characterization of these functional isocyanide complexes. The spectroscopic properties (^{13}C NMR and IR) of the new ligand are discussed by coomparison with carbon monoxide and various other two-electron ligands ($CNCH_3$, CS, $P(OPh)_3$, ...). Two modes of access to optically active diastereoisomers of chiral chromium are also presented.

Experimental Section

General Procedures and Starting Materials. Infrared spectra were recorded on a Beckman IR 12 spectrophotometer. Frequencies are accurate to ±2 cm^{-1}. ^1H NMR spectra were recorded on a Varian EM 360 (^1H, $CDCl_3$ solution with Me_4Si internal standard unless otherwise noted) and ^{13}C NMR spectra were recorded on a Brucker WP 80 DF ($CDCl_3$, reference Me_4Si). Mass spectra were determined at 70 eV by using a Varian MAT 311 double-focusing spectrometer. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter. All new compounds gave satisfactory elemental analyses (C, H, N). All the (arene)tricarbonylchromium derivatives were synthetized by published procedures.[7] The optically active **1R** (methyl *m*-methoxybenzoate)tricarbonylchromium [$[\alpha]^{25}{}_D$ +156° (*c* 1.4, $CHCl_3$)] was obtained as previously reported[8] and neomenthyldiphenylphosphine is commercially available [$[\alpha]^{25}{}_D$ +87.4° (*c* 1.57, CH_2Cl_2), Strem].

Photochemical reactions were carried out in a 200-cm^3 Pyrex vessel fitted with a water-cooled quartz finger. The UV source (TQ 150 Hanau high-pressure mercury lamp) was located inside the finger.

Syntheses. (Ar)$Cr(CO)_2$(CNCOPh) (3a, Ar = $PhCO_2CH_3$; 3b, Ar = *o*-$OCH_3C_6H_4CO_2CH_3$; 3c, Ar = *m*-$OCH_3C_6H_4CO_2CH_3$; 3d, Ar = C_6H_6; 3e, Ar = $C_6(CH_3)_6$). The preparation of all the compounds follows the same procedure. In a typical experiment, 2 g of ($PhCO_2CH_3$)$Cr(CO)_3$ (7.35 × 10^{-3} mol) and 1 g of KCN (1.54 × 10^{-2} mol) in 200 mL of deoxygenated methanol were irradiated under nitrogen for 3 h. After vacuum evaporation of the solvent, the anion ($PhCO_2CH_3$)$Cr(CO)_2CN^-$ (**2**) (IR (CH_2Cl_2) ν(C≡O) 1910, 1830 cm^{-1}; ^1H NMR (CD_3COCD_3) $\delta(C_6H_5Cr)$ 5.82 (m, 2), 5.12 (m, 1), 4.84 (m, 2), $\delta(OCH_3)$ 3.47 (s, 3)) was allowed to react with 1 g of PhCOCl (7.1 × 10^{-3} mol) followed by immediate addition of 20 mL of CH_2Cl_2. After TLC purification (silica gel; eluant ether–petroleum ether, 1:4), a 2.26-g sample of **3a**, (η-$PhCO_2CH_3$)$Cr(CO)_2$CNCOPh, was isolated: mp 78 °C; ^1H NMR ($CDCl_3$) $\delta(C_6H_5)$ 8.45 (m, 2), 7.90 (m, 3), $\delta(C_6H_5Cr)$ 6.45 (m, 2), 5.65 (m, 3), $\delta(OCH_3)$ 4.05 (s, 3); mass spectrum, *m/e* (relative intensity) 375 (7), 344 (15), 319 (15), 272 (1.6), 188 (12), 155 (1.2), 136 (55), 105 (100), 77 (70), 52 (10); yield 81%. Anal. Calcd: C, 57.60; H, 3.46; N, 3.73. Found: C, 57.24; H, 3.52; N, 3.86.

(*o*-$OCH_3C_6H_4CO_2CH_3$)$Cr(CO)_2$(CNCOPh) (3b): oil; ^1H NMR $\delta(C_6H_5)$ 8.5 (m, 2), 7.86 (m, 3), $\delta(C_6H_4Cr)$ 6.6 (d, 1), 6.0 (t, 1), 5.3 (q, 2), $\delta(OCH_3)$ and δ (CO_2CH_3) 4.0 (s, 6).

(*m*-$OCH_3C_6H_4CO_2CH_3$)$Cr(CO)_2$(CNCOPh) (3c): oil; ^1H NMR $\delta(C_6H_5)$ 8.3 (m, 2), 7.9 (m, 3), $\delta(C_6H_4Cr)$ 5.9 (m, 4), $\delta(OCH_3)$ and $\delta(CO_2CH_3)$ 3.9 (s, 3), 4.1 (s, 3). If the optically active tricarbonyl complex [$[\alpha]^{25}{}_D$ +156° (*c* 1.4, $CHCl_3$)] is used instead of the racemic complex under the conditions described above, the benzoyl isocyanide (oil) shows an optical rotation of $[\alpha]^{25}{}_D$ +133° (*c* 1.09, $CHCl_3$). The absolute configuration is shown in Scheme III. In this reaction, the planar chirality **1R** due to the complex disubstituted arene ring remains untouched, so the absolute configuration of isocyanide complex can be ascertained by correlation to that of the tricarbonyl complex. Mass spectrum, *m/e* (relative intensity): 405 (16), 374 (1), 349 (38), 302 (0.8), 218 (96), 166 (77), 105 (100), 77 (86), 52 (46).

(C_6H_6)$Cr(CO)_2$(CNCOPh) (3d): mp 104 °C; ^1HNMR $\delta(C_6H_5)$ 8.3 (m, 2), 7.7 (m, 3), $\delta(C_6H_6)$ 5.6 (s, 6).

[$C_6(CH_3)_6$]$Cr(CO)_2$(CNCOPh) (3e): mp 144 °C; ^1H NMR δ-(C_6H_5) 8.4 (m, 2), 7.7 (m, 3), $\delta(CH_3)$ 2.33 (s, 18).

($PhCO_2CH_3$)$Cr(CO)_2$($CNCH_3$) (4). One gram of ($PhCO_2CH_3$)$Cr(CO)_3$ (3.7 × 10^{-3} mol) and 0.5 g of KCN (0.77 × 10^{-2} mol in 200 mL of deoxygenated methanol were irradiated under nitrogen for 1 h. After vacuum evaporation of the solvent, $PhCO_2CH_3Cr(CO)_2CN^-$ was allowed to react with 0.2 g of methyl fluorosulfonate (Aldrich's Magic Methyl (toxic)) (1.7 × 10^{-2} mol) followed by immediate addition of 20 mL of CH_2Cl_2. After TLC purification (eluant ether–petroleum ether, 1:3), a 0.77-g sample of **4** was isolated: yield 75%; mp 125 °C; ^1H NMR $\delta(C_6H_5Cr)$ 6.0 (d, 2), 5.2 (m, 3), $\delta(OCH_3)$ 4.0 (s, 3), $\delta(NCH_3)$ 3.4 (s, 3). Anal. Calcd: C, 50.52; H, 3.85; N, 4.91. Found: C, 50.68; H, 3.89; N, 4.86.

($PhCO_2CH_3$)Cr(CO)(CNCOPh)$P(OPh)_3$ (5). A 1.5-g sample (4 × 10^{-3} mol) of **3a** and 3.1 g (10^{-2} mol) of $P(OPh)_3$ dissolved in 200 mL of benzene were irradiated for 1 h at room temperature under a nitrogen stream. Filtration and removal of the solvent were followed by chromatography on 10 silica-gel preparative TLC plates (Kieselgel G, Typ GO, Merck) using a 1:1 ether–petroleum ether mixture as eluant. Two bands were developed, corresponding respectively to ($PhCO_2CH_3$)Cr(CO)(CNCOPh)$P(OPh)_3$ (**5**) [0.66 g, yield 25%, mp 77–78 °C; IR ν(C≡O) 1930 cm^{-1}; ^1H NMR $\delta(C_6H_5CO)$ 8.45 (m, 2), 7.8 (m, 3), $\delta(C_6H_5O)$ 7.55 (m, 15), $\delta(C_6H_5Cr)$ 5.1–5.9 (m, 5), $\delta(OCH_3)$ 3.85 (s, 3)] and to the starting material (0.2 g). Anal. Calcd: C, 63.93; H 4.26; N, 2.13. Found: C, 64.41; H, 4.41; N, 2.05.

($PhCO_2CH_3$)$Cr(CO)_2P(OPh)_3$ (6). A mixture of **4** (1 g; 3.5 × 10^{-3} mol) and 3.1 g (10^{-2} mol) of P $(OPh)_3$ dissolved in 200 mL of benzene were irradiataed for 45 min under nitrogen. After concentration under vacuum and chromatography in silica gel (eluant 1:2 ether–petroleum ether), 1.8 g (3.2 × 10^{-3} mol) of complex **6** (mp 85 °C'; IR (CCl_4) $\bar{\nu}$(C≡O) 1944, 1893 cm^{-1}; yield 91%) was isolated. Anal. Calcd: C, 60.65; H, 4.18. Found: C, 61.01; H, 4.09.

($PhCO_2CH_3$)Cr(CO)(CNCOPh)PPh_2(neomenthyl) (7A and 7B). A 0.75-g amount (2 × 10^3 mol) of **3a** and 1.62 g (5 × 10^{-3} mol) of neomenthyldiphenylphosphine ($[\alpha]^{25}{}_D$ +87.4 (*c* 1.57, CH_2Cl_2)) in C_6H_6 were irradiated for 50 min. The red-orange solution rapidly became purple. Filtration and removal of the solvent were followed by chromatography on 15 silica-gel preparative TLC plates using benzene as the eluant. Three bands were developed, corresponding respectively to the starting material (0.15 g, 0.4 10^{-3} mol) diastereoisomer **7A** [oil; 0.21 g, 0.43 10^{-3} mol; $[\alpha]^{25}{}_D$ +60° (*c* 10, pentane)] and diastereoisomer **7B** [oil; 0.08 g, 0.12 10^{-3} mol; $[\alpha]^{25}{}_D$ +81° (*c* 1.3, pentane); yield 27%]. IR of **7A** and **7B** (pentane): ν(C≡O) 1918, $\nu(CO_2CH_3)$ 1745, ν(C=O) (CNCOPh) 1640 cm^{-1}.

(*m*-$OCH_3C_6H_4CO_2CH_3$)Cr(CO)(CNCOPh)$P(OPh)_3$ (8A and 8B). A mixture of optically active **3c** (0.8 g, 2 × 10^{-3} mol) and triphenyl phosphite (3.1 g, 10^{-2} mol) dissolved in benzene was irradiated for 40 min. Removal of the solvent was followed by chromatography on silica-gel TLC plates using benzene as eluant. Two bands were developed, corresponding respectively to **8A** [oil; 0.22 g, 0.32 × 10^{-3} mol; ^1H NMR (C_6D_6) $\delta(OCH_3)$ 3.15 (s, 3), $\delta(CO_2CH_3)$ 3.48 (s, 3), $\delta(C_6H_4Cr)$ 4.1 (m, 1), 4.7 (m, 1), 4.9 (q, 1), 5.6 (m, 1); $[\alpha]^{25}{}_D$ +132° (*c* 1.09, pentane)] and **8B** [oil; 0.21 g, 0.32 × 10^{-3} mol; ^1H NMR (C_6D_6) $\delta(OCH_3)$ 2.96 (s, 3), $\delta(CO_2CH_3)$ 3.71 (s, 3), $\delta(C_6H_4Cr)$ 3.9 (m, 1), 4.5 (m, 1), 5.01 (q, 1), 5.54 (m, 1); $[\alpha]^{25}{}_D$ +115° (*c* 1.3, pentane); yield 32%]. IR of **8A** and **8B** (pentane): $\bar{\nu}$(C≡O) 1932, $\bar{\nu}(CO_2CH_3)$ 1745, $\bar{\nu}$(C=O) (CNCOPh) 1670 cm^{-1}.

Results and Discussion

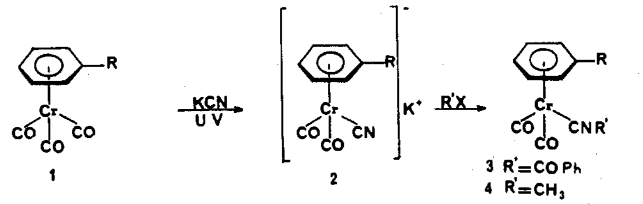
Synthesis of (arene)$Cr(CO)_2$CNR Complexes. Since alkylation of cyanide complexes has been previously used to prepare metal isocyanides,[9,10] we attempted synthesis of N-substituted isocyanides via electrophilic attack of benzoyl halide on metal cyanide ions. Scheme I outlines the general

Table I. Yields and IR and ^{13}C NMR Spectra of Complexes of the Type (arene)Cr(CO)$_2$CNR′

complex	arene ligand	R′	yields, %	IR,^{a} cm^{-1}		^{13}C NMR^c		
				$\bar{\nu}$(≡O)	$\bar{\nu}$(C=O)	δ(C≡O)	δ(C≡NR)^d	δ(C=N-^{13}COPh)
3a	methyl benzoate	COPh	81	1977, 1922	1680	231.6	223.8	157
3b	methyl *o*-methoxybenzoate	COPh	72	1986, 1915	1670			
3c	methyl *m*-methoxybenzoate	COPh	63	1980, 1917	1670	232	226	157.3
3d	benzene	COPh	84	1970, 1895	1660	233.4	232.6	158.9
3e	hexamethylbenzene	COPh	90	1955, 1883	1650	236.1	242.4	160.3
4	methyl benzoate	CH$_3$^{b}	75	1939, 1891		236.5	180.7	

^{a} Solvent CCl$_4$; $\bar{\nu}$(C≡N) was not observed for all CNCOPh complexes; IR of free CNCOPh (CHCl$_3$): $\bar{\nu}$(C≡N) 2100, $\bar{\nu}$(C=O) 1738 cm^{-1}.[12] ^{b} $\bar{\nu}$(C≡N) 2080 cm^{-1}. ^{c} Positive chemical shifts in ppm downfield from Me$_4$Si, chloroform solution. ^{d} $\delta_{^{13}\mathrm{C}}$(free ^{13}CNCOPh) 165;[12] $\delta_{^{13}\mathrm{C}}$(Cr(CO)$_5$^{13}CNCOPh) 186.5;[10] $\delta_{^{13}\mathrm{C}}$(free ^{13}CNCH$_3$) 156.6.

Scheme I

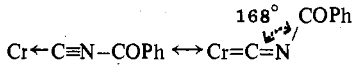


preparation of (η-arene)Cr(CO)$_2$(CNCOPh) derivatives from (η-arene)Cr(CO)$_3$ complexes.[7] The air-sensitive monocyanide intermediates, generated by UV irradiation in the presence of KCN, were treated with benzoyl chloride at room temperature (R′ = COPh, Scheme I). Extension of this reaction with methyl iodide provides methyl isocyanide complexes (R′ = CH$_3$). The yields and spectroscopic characterization are given in Table I.

Spectroscopic Studies. Mass Spectra. The stronger bonding of the Cr–CNR′ linkage compared to Cr–CO ones, well recognized in alkyl or aryl isocyanide cationic complexes,[11] also appears evident in the mass spectra of complexes **3a** and **3c**. One of the prominent ions is always [(arene)Cr(CNCOPh)]$^+$, and loss of CO invariably precedes loss of CNCOPh. The mass spectrum of Cr(CO)$_5$(CNCOPh), previously reported,[10] showed similar behavior. Therefore, it may be assumed that the CNCOPh ligand is a better σ donor than CO since σ character is the main bonding component when positively charged species are involved. A peak corresponding to mass of free benzoyl isocyanide is not observed, in agreement with its thermal instability.[12]

^{13}C NMR Studies. The ^{13}C NMR spectra of (benzoyl isocyanide)chromium complexes of the type ArCr(CO)$_2$(CNCOPh) (Ar = arene) (**3a**, **3b**, **3c**, **3d**, **3e**) exhibit in the low-field portion two distinct carbon resonances with a relative intensity of 1:2, which are due to the isocyanide carbons and the two equivalent carbonyls, respectively. The ^{13}C NMR shifts of ^{13}CNCOPh (220–240 ppm) and CN^{13}COPh ($\simeq$158 ppm) can be readily distinguished and assigned in the ^{13}C-(^{1}H)-coupled spectrum. The CN^{13}COPh resonance is split into a triplet (for instance, ^3J(CH) = 5.5 Hz in **3d**) whereas only a singlet appears for the ^{13}CNCOPh resonance. As shown in Table I, the isocyanide carbon atom resonance shifts to lower field compared to the free ligand (free δ(^{13}CNCOPh) 165[12]); 20 ppm by Cr(CO)$_5$ complexation[10] and 60–79 ppm by ArCr(CO)$_2$ complexation. The ^{13}CNCH$_3$ carbon resonance shows only a 24-ppm downfield shift by (PhCO$_2$CH$_3$)Cr(CO)$_2$ complexation (free δ(^{13}CNCH$_3$) 156.6;[13] **4** δ(^{13}CNCH$_3$) 180.7).

However, the most striking feature is the greater electronic susceptibility of the benzoyl isocyanide carbon resonance compared to that of the carbon monoxide resonance. The replacement of the methyl benzoate ligand (**3a**) by a hexamethylbenzene group (**3e**) causes a 19-ppm downfield shift in the isocyanide carbon resonance but only a 4.5-ppm downfield shift in the carbonyl carbon resonance. The electron-donor group appears to have a dominant deshielding effect on the isocyanide resonance relative to that of the carbonyl group. This effect underlines the importance of resonance structure b in agreement with the carbene-like shift[14] and the previous X-ray investigation (α = 168°).[6]


$$\mathrm{Cr{\leftarrow}C{\equiv}N{-}COPh} \longleftrightarrow \mathrm{Cr{=}C{=}N{-}COPh}$$

a b

Table II. Carbon Monoxide Stretching Frequencies and Calculated Cotton–Kraihanzel Stretching Force Constant of Complexes of the Type (PhCO$_2$CH$_3$)Cr(CO)$_2$L

L	$\bar{\nu}$(C≡O),^{a} cm^{-1}	k, mdyn/Å
CS^b	1992–1939	15.60
CNCOPh	1987–1922	15.43
CO	1994–1928	15.36
P(OPh)$_3$	1944–1893	14.87
CNCH$_3$	1931–1891	14.81
PPh$_3$^{b}	1923–1871	14.53

^{a} Solvent CCl$_4$. ^{b} Reference 3.

Furthermore, substitution of C≡O by CNCH$_3$, which is a better net electron donor than CO, causes a downfield shift of ancillary carbonyl atoms (**3a** δ(^{13}CO) 231.6, **4** δ(^{13}CO) 236.5). These data are consistent with the previous suggestion[15] that the carbonyl resonance is deshielded by increasing electron density at the transition metal. Finally, it is of interest to note the close similarity between δ(^{13}C≡O) in (PhCO$_2$CH$_3$)Cr(CO)$_3$ (δ(^{13}CO) 231.2)[15] and δ(^{13}CO) in **3a** (δ^{13}CO) 2.31.6). These results suggest that *N*-acyl isocyanides have ligating properties (net σ:π electron-withdrawing ability) close to those of carbonyl.

Infrared Studies. It is known that the electron density in ArCr(CO)$_3$ complexes may be varied considerably by the nature of ring substituents attached to the benzene ring.[16] This is clearly reflected in the C≡O stretching frequencies of these complexes.[16] A very similar influence of the ligand L is observed in the ArCr(CO)$_2$L series (Table II). It is interesting to note that the ν(C≡O) frequencies do not show a significant shift upon substitution of CO by CNCOPh while CNCH$_3$ complexation decreases notably the C≡O stretching frequencies of complex **4**. As the C≡O stretching frequencies belong to different symmetry species, it is more appropriate to compare stretching force constants k(C≡O) calculated according to the Cotton–Kraihanzel[17] approximation for the two cases of local symmetry C_{3v} (ArCr(CO)$_3$) and C_{2v} (ArCr(CO)$_2$L). Table II presents some methyl benzoate complexes of the general type C$_6$H$_5$CO$_2$MeCr(CO)$_2$L for which stretching force constants have been determined. It is quite clear from this list that the net donor–acceptor properties of the CNCOPh ligand are quite similar to those of CO.

Participation of the CNCOPh ligand in metal–ligand back-bonding may also be deduced from the C≡O stretching

Scheme II

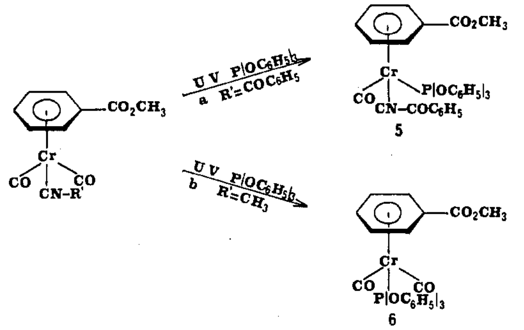
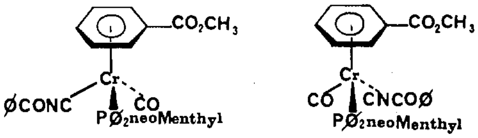


Chart I



7A + 7B

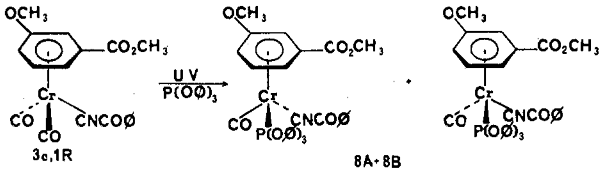
absorptions of the benzoyl isocyanide group which are lower in the ArCr(CO)$_2$CNCOPh complexes than in a free ligand.[12] This significant lowering in frequency on complexation ($\Delta\nu$ = 88 cm^{-1} in **3e**) suggests that the ketone moiety receives a good deal of the charge which is transferred from the chromium to the benzoyl isocyanide ligand. The decrease is largest when electron-donating substituents on the π-benzene ring raise the electron density in the ArCr(CO)$_2$CNCOPh complex. Nevertheless, even in complex **3a** ($\Delta\nu$ = 58 cm^{-1}), this effect could be enough to strengthen significantly the Cr–CNCOPh bond.

The C≡N stretching absorptions of the benzoyl isocyanide group should also be lower, but, unfortunately, ν(C≡N) was not observed for coordinated CNCOPh (**3a–e**). Isocyanide stretching absorption may be weak or shifted so much to lower energy[18] that it is under the C≡O stretches. This later suggestion could explain the enlargement of the lowest carbonyl frequency but a definitive conclusion is difficult without additional data.

Syntheses of Chiral Complexes. Irradiation of (PhCO$_2$CH$_3$)Cr(CO$_2$(CNCOPh) (**3a**) in benzene solvent in the presence of P(OPh)$_3$ resulted in selective CO photodissociation with a concomitant production of the (PhCO$_2$CH$_3$)Cr(CO)(CNCOPh)P(OPh)$_3$ complex. In contrast to CO photolabilization, photochemical reaction of (PhCO$_2$CH$_3$)Cr(CO)$_2$(CNCH$_3$) (**4**), under the above conditions, afforded substitution of methyl isocyanide by P(OPh)$_3$ (Scheme II). These results are in agreement with spectroscopic studies and confirm that the order of increasing strength of the chromium–ligand bond is CNCH$_3$ < CO < CNCOPh.

Extension of the former reaction to the optically active phosphine PPh$_2$(neomenthyl) instead of P(OPh)$_3$ provides a pair of diastereoisomers (**7A** and **7B**) which differ only in the configuration at the metal atom (Chart I). Both isomers **7A** [$[\alpha]^{25}_{\rm D}$ +60 (pentane)] and **7B** [$[\alpha]^{25}_{\rm D}$ +81° (pentane)] show different NMR spectra [**7A** δ(CO$_2$CH$_3$) 3.49, **7B** δ(CO$_2$CH$_3$) 3.45; solvent C$_6$D$_6$] and can be separated by chromatography on silica gel (see Experimental Section). The relative amounts of the products depend on irradiation time: for example, the **A**:**B** ratio is 27/73 after 50 min while, after 2 h, the **A**:**B** ratio is 50/50 (**3a**, 2 × 10^{-3} mol). Both diastereoisomers are configurationally stable in benzene or pentane solution.

Scheme III



(Methyl m-methoxybenzoate)tricarbonylchromium ($[\alpha]^{25}_{\rm D}$ +156°), **1R**, serves as the starting material[8] for another series of optically active organometallic compounds. Unlike in complexes **5**, **7A**, and **7B**, the metal atom is not the center of asymmetry in this derivative but instead the asymmetry is based in the arene ligand. After resolution of planar chirality which is now well-known,[8] substitution of C≡O by :CNCOPh affords optically active (methyl m-methoxybenzoate(benzoyl isocyanide)dicarbonylchromium (**3c** ($[\alpha]^{25}_{\rm D}$ +133°). Irradiation of **3c**, in the presence of P(OPh)$_3$, results in displacement of one of the two carbon monoxide ligands and affords a pair of diastereoisomers **8A** ($[\alpha]^{25}_{\rm D}$ +132°) and **8B** ($[\alpha]^{25}_{\rm D}$ +115°) which can again be resolved into pure isomer by chromatography on silica gel. Like the corresponding chiral phosphine diastereoisomers, **8A** and **8B** are also configurationally stable in benzene solution (Scheme III). The dynamic stereochemistry of these optically active complexes is under investigation.

Registry No. **3a**, 67359-46-0; **3b**, 71230-26-7; **3c**, 71275-46-2; **3c, 1R**, 71230-25-6; **3d**, 71230-24-5; **3e**, 71230-23-4; **4**, 71230-22-3; **5**, 71230-21-2; **6**, 63928-77-8; **7A**, 71275-45-1; **7B**, 71230-20-1; **8A**, 71250-48-1; **8B**, 71300-59-9; (PhCO$_2$CH$_3$)Cr(CO)$_3$, 12125-87-0; (o-OCH$_3$C$_6$H$_4$CO$_2$CH$_3$)Cr(CO)$_3$, 12182-02-4; (m-OCH$_3$C$_6$H$_4$CO$_2$CH$_3$)Cr(CO)$_3$, 12153-80-9; (+)-(m-OCH$_3$C$_6$H$_4$CO$_2$CH$_3$)Cr(CO)$_3$, 33111-38-5; (C$_6$H$_6$)Cr(CO)$_3$, 12082-08-5; [C$_6$(CH$_3$)$_6$]Cr(CO)$_3$, 12088-11-8.

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(18) Owing to the acceptor ability of benzoyl substituent, structure b will be favored with a consequent lowering of the bond order and a decrease in the CN stretching frequency. For a discussion of this effect see L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley, New York, 1969.