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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Homoleptic Seven- and Six-Coordinate Alkyl Isocyanide Complexes of Chromium: Synthesis, Characterization, and Redox and Substitution Chemistry

WILLIAM S. MIALKI, DAVID E. WIGLEY, THOMAS E. WOOD, and RICHARD A. WALTON*

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The treatment of ethanolic solutions of chromium(II) with alkyl isocyanides RNC (R = CMe_3 or C_6H_{11}) in the presence of KPF_6 produces in high yield the yellow crystalline complexes $[Cr(CNR)_6](PF_6)_2$. These low-spin chromium(II) species ($t_{2g}{}^4$ ground state) are converted to diamagnetic seven-coordinate $[Cr(CNR)_7](PF_6)_2$ by neat RNC. This novel increase in coordination number from six to seven completes the first homologous series of homoleptic seven-coordinate complexes of any transition group (Cr, Mo, and W). In polar nonaqueous solvents, $[Cr(CNR)_7](PF_6)_2$ reverts to $[Cr(CNR)_6](PF_6)_2$ through release of RNC, a change which may be monitored conveniently by ^1H NMR spectroscopy and cyclic voltammetry. A comparison of the voltammetric half-wave potentials of $[Cr(CNR)_6](PF_6)_2$ with those for $[Cr(CNPh)_6](PF_6)_2$ permits a measure of the differences in thermodynamic stability of the various oxidation states of $[Cr(CNR)_6]^{n+}$ and $[Cr(CNPh)_6]^{n+}$. While the oxidation $Cr^{2+} \rightarrow Cr^{3+}$ is more favored in the alkyl derivatives, the reductions $Cr^{2+} \rightarrow Cr^+$ and $Cr^+ \rightarrow Cr^0$ are clearly less favored. Both the six- and seven-coordinate homoleptic alkyl isocyanide complexes react with tertiary phosphines PR_3 (R = Et, *n*-Pr, or *n*-Bu) and with 1,2-bis(diphenylphosphino)ethane (dppe) to form the paramagnetic species *trans*-$[Cr(CNR)_4(PR_3)_2](PF_6)_2$ and *cis*-$[Cr(CNR)_4(dppe)](PF_6)_2$. The dppe complexes react with neat RNC to form $[Cr(CNR)_5(dppe)](PF_6)_2$. Detailed studies of the electrochemistry of the mixed-ligand complexes have been carried out.

Introduction

The reactions of dinuclear multiply bonded complexes of molybdenum, tungsten, and rhenium with the π-acceptor ligands CO, NO, and RNC can provide a convenient high-yield synthetic route to mononuclear complexes that are often not as readily accessible by other synthetic methods.[1] Following our earlier studies involving the cleavage of the Re–Re triple bond of $Re_2X_4(PR_3)_4$ (X = Cl or Br) by CO to produce $Re(CO)_2X_2(PR_3)_2$[2] and the corresponding conversion of $Mo_2X_4(PR_3)_4$, containing a Mo–Mo quadruple bond, to $Mo(NO)_2X_2(PR_3)_2$ by NO,[3] we turned our attention to the reactions of multiply bonded complexes with alkyl and aryl isocyanides. As a consequence, we were able to show that quadruply bonded molybdenum and tungsten complexes ($Mo_2(O_2CCH_3)_4$, $K_4Mo_2Cl_8$, $Mo_2Cl_4(PR_3)_4$, and $W_2(mhp)_4$, where mhp is the anion of 2-hydroxy-6-methylpyridine, can be converted easily to the seven-coordinate species $[Mo(CNR)_7](PF_6)_2$, $[Mo(CNR)_{7-x}(PR_3)_x](PF_6)_2$ (x = 1, 2), and $[W(CNR)_7](PF_6)_2$.[4-6]

Actually, the first cleavage of a metal–metal quadruple bond by an organic isocyanide, phenyl isocyanide to be exact, was accomplished back in 1952 when $Cr_2(O_2CCH_3)_4{\cdot}2H_2O$ was found[7] to form $Cr(CNPh)_6$ upon reaction with PhNC. This was, of course, several years before the recognition of the existence of multiple metal–metal bonds[8] so that the significance of this reaction was not fully realized at the time. This reaction is now recognized[1] as being an example of a reductive cleavage of the Cr–Cr quadruple bond; comparable examples in molybdenum and tungsten chemistry are the conversions of $Mo_2(O_2CCH_3)_4$ and $W_2(dmhp)_4$ (dmhp is the anion of 2,4-dimethyl-6-hydroxypyrimidine) to $Mo(CNPh)_6$ and $W(CNPh)_6$.[9,10]

The possibility that the nonreductive cleavage of $Cr_2(O_2CCH_3)_4{\cdot}2H_2O$ by alkyl isocyanides would afford the previously unknown chromium(II) species $[Cr(CNR)_6]^{2+}$ or $[Cr(CNR)_7]^{2+}$ has led us to study these systems. While we were unable to isolate complexes of these types by this means, or by the alternative procedure of using the quadruply bonded complex $Cr_2(mhp)_4$,[11] we have subsequently prepared the complexes $[Cr(CNR)_6](PF_6)_2$ and $[Cr(CNR)_7](PF_6)_2$, where R = CMe_3 or C_6H_{11}, by an alternative route. We now describe details of the synthesis of these new classes of chromium(II) complexes together with a full account of their spectroscopic properties and substitution reactions with tertiary phosphines. Preliminary details of this work have been reported previously.[12]

Experimental Section

Starting Materials. The alkyl isocyanides were prepared by standard literature procedures.[13] Monodentate tertiary phosphines, 1,2-bis(diphenylphosphino)ethane (abbreviated dppe), and other reagents and solvents were obtained from commerical sources and were used as received.

Reaction Procedures. All reactions were carried out with a nitrogen atmosphere, and all solvents were deoxygenated prior to use by purging with N_2 gas.

(A) Reactions of Ethanolic Solutions of Chromium(II). (i) $[Cr(CNC(CH_3)_3)_6](PF_6)_2$. A freshly prepared ethanolic solution of chromium(II)[14] (prepared from 1 g of $CrCl_3{\cdot}6H_2O$ dissolved in 60 mL of ethanol) was added dropwise under nitrogen to a stirred solution containing an excess of *tert*-butyl isocyanide (4.0 mL, 38 mmol) and KPF_6 (0.83 g, 4.5 mmol) in 15 mL of ethanol. After these reagents were mixed, the color of the solution changed immediately from sky blue to yellow. After the reaction mixture had stirred for 30 min, the light yellow precipitate was filtered off, washed with water, 2-propanol, and diethyl ether, and dried in vacuo; yield 2.34 g (74%). Anal. Calcd for $C_{30}H_{54}CrF_{12}N_6P_2$: C, 42.86; H, 6.47; N, 10.00. Found: C, 43.09; H, 6.75; N, 10.28.

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(ii) $[Cr(CNC_6H_{11})_6](PF_6)_2$. This yellow complex was prepared by a procedure analogous to section A(i) using cyclohexyl isocyanide in place of *tert*-butyl isocyanide; yield 51%. Anal. Calcd for $C_{42}H_{66}CrF_{12}N_6P_2$: C, 50.60; H, 6.67; N, 8.43. Found: C, 50.36; H, 6.59; N, 8.20.

(B) Reactions of $[Cr(CNR)_6](PF_6)_2$. (i) $[Cr(CNC(CH_3)_3)_7](PF_6)_2$. *tert*-Butyl isocyanide (0.60 mL, 5.7 mmol) was syringed into a test tube containing a quantity of the six-coordinate complex $[Cr(CNC(CH_3)_3)_6](PF_6)_2$ (0.50 g, 0.60 mmol). The clear solution was stirred and allowed to stand under nitrogen for 45 min. Diethyl ether was then added, and the solid which precipitated was washed with water, 2-propanol, and diethyl ether and dried in vacuo; yield 97%. Anal. Calcd for $C_{35}H_{63}CrF_{12}N_7P_2$: C, 45.50; H, 6.87; N, 10.61. Found: C, 45.59; H, 6.98; N, 10.77. This product is slightly soluble in methanol and ethanol, is very soluble in dichloromethane, and decomposes rapidly in acetone.

An alternative procedure for the preparation of this complex is as follows. A freshly prepared ethanolic solution containing 1 g of $CrCl_3 \cdot 6H_2O$ dissolved in 20 mL of ethanol was passed through a Jones reductor and added dropwise to a stirred mixture of *tert*-butyl isocyanide (8.0 mL, 76 mmol) and KPF_6 (0.83 g, 4.5 mmol). Upon mixing of the ingredients, an orange-yellow precipitate formed. This solid was shown by its spectroscopic properties to be identical with $[Cr(CNC(CH_3)_3)_7](PF_6)_2$ as prepared above.

(ii) $[Cr(CNC_6H_{11})_7](PF_6)_2$. A bright yellow complex of this stoichiometry was obtained by the reaction of $[Cr(CNC_6H_{11})_6](PF_6)_2$ with *neat* cyclohexyl isocyanide from a procedure analogous to that of section B(i); yield 89%. Anal. Calcd for $C_{49}H_{77}CrF_{12}N_7P_2$: C, 53.21; H, 7.02; N, 8.86. Found: C, 53.43; H, 7.17; N, 8.67. This complex can also be prepared from $CrCl_3 \cdot 6H_2O$ as described in section B(i).

(C) Reactions of $[Cr(CNC(CH_3)_3)_7](PF_6)_2$ and $[Cr(CNC(CH_3)_3)_6](PF_6)_2$ with Tertiary Phosphines. (i) $[Cr(CNC(CH_3)_3)_4(P(C_2H_5)_3)_2](PF_6)_2$. A quantity of $[Cr(CNC(CH_3)_3)_6](PF_6)_2$ (0.231 g) was added to a round-bottom flask that was evacuated and filled with dry-nitrogen gas. To this were added 7 mL of deoxygenated ethanol and 0.2 mL of triethylphosphine. The reaction mixture was heated at 65 °C for 1 h and allowed to cool to room temperature. Addition of 10 mL of diethyl ether produced an orange-yellow solid; yield 0.204 g (82%). Anal. Calcd for $C_{32}H_{66}CrF_{12}N_4P_4$: C, 42.20; H, 7.30; N, 6.15. Found: C, 42.50; H, 7.16; N, 6.08. The product can be recrystallized from dichloromethane–diethyl ether mixtures.

The reaction of $[Cr(CNC(CH_3)_3)_7](PF_6)_2$ with $P(C_2H_5)_3$ as outlined above produced an identical product; yield 90%.

Dichloromethane can be used in place of ethanol in these reactions with a corresponding change in reaction time (15 min). This modified procedure was found to produce the pure complex in high yield.

(ii) $[Cr(CNC(CH_3)_3)_4(P(C_3H_7)_3)_2](PF_6)_2$. This yellow-orange complex was obtained from the reaction between $[Cr(CNC(CH_3)_3)_7](PF_6)_2$ and tri-*n*-propylphosphine in CH_2Cl_2 by a procedure analogous to that of section C(i); yield 71%. Anal. Calcd for $C_{38}H_{78}CrF_{12}N_4P_4$: C, 45.87; H, 7.90. Found: C, 45.62; H, 7.84.

(iii) $[Cr(CNC(CH_3)_3)_4(P(C_4H_9)_3)_2](PF_6)_2$. This yellow compound was obtained by a procedure analogous to that of section C(i) using ethanol as solvent; yield 57%. Anal. Calcd for $C_{44}H_{90}CrF_{12}N_4P_4$: C, 48.98; H, 8.41. Found: C, 48.50; H, 8.25.

(iv) $[Cr(CNC(CH_3)_3)_4(dppe)](PF_6)_2$. The six-coordinate complex $[Cr(CNC(CH_3)_3)_6](PF_6)_2$ (0.216 g) was dissolved in 7 mL of ethanol and mixed with 0.40 g of 1,2-bis(diphenylphosphino)ethane. The resultant solution was heated to 65 °C for 1 h and then cooled to room temperature. Addition of diethyl ether produced a bright yellow precipitate which was washed with diethyl ether and vacuum dried; yield 43%. It was recrystallized from methylene chloride–diethyl ether mixtures. Anal. Calcd for $C_{46}H_{60}CrF_{12}N_4P_4$: C, 51.50; H, 5.63; N, 5.21. Found: C, 51.57; H, 5.62; N, 5.02.

This complex can also be prepared by an analogous procedure starting from $[Cr(CNC(CH_3)_3)_7](PF_6)_2$; yield 70%.

(D) Reactions of $[Cr(CNC_6H_{11})_6](PF_6)_2$ with Tertiary Phosphines. (i) $[Cr(CNC_6H_{11})_4(PR_3)_2](PF_6)_2$. Complexes of this type (R = C_2H_5, C_3H_7 or C_4H_9) were prepared by the reaction between $[Cr(CNC_6H_{11})_6](PF_6)_2$ and PR_3 in dichloromethane with a procedure analogous to that of section C(i). The complexes were obtained in yields of 92% (R = C_2H_5), 73% (R = C_3H_7), and 50% (R = C_4H_9) and were characterized on the basis of their spectroscopic and electrochemical properties which were similar to those of their *tert*-butyl isocyanide analogues.

(ii) $[Cr(CNC_6H_{11})_4(dppe)](PF_6)_2$. This orange complex was prepared by a procedure analogous to that of section C(iv) with ethanol as the reaction solvent; yield 47%. Its identity was confirmed by its spectroscopic properties.

(E) Conversion of $[Cr(CNC(CH_3)_3)_4(dppe)](PF_6)_2$ to $[Cr(CNC(CH_3)_3)_5(dppe)](PF_6)_2$. The six-coordinate complex $[Cr(CNC(CH_3)_3)_4(dppe)](PF_6)_2$ (0.256 g) was placed in a test tube and to it was added sufficient *tert*-butyl isocyanide to form a slurry. This was stirred vigorously for 5 min. After this period of time, the solid had changed from a light yellow to dark orange. The resulting orange complex was filtered off and washed with diethyl ether; yield 90%. Anal. Calcd for $C_{51}H_{69}CrF_{12}N_5P_4$: C, 52.99; H, 6.01. Found: C, 52.73; H, 5.98. Note, use of a large excess of isocyanide may result in further reaction to produce the homoleptic seven-coordinate complex $[Cr(CNC(CH_3)_3)_7](PF_6)_2$.

(F) Conversion of $[Cr(CNC_6H_{11})_4(dppe)](PF_6)_2$ to $[Cr(CNC_6H_{11})_5(dppe)](PF_6)_2$. Like its *tert*-butyl isocyanide analogue, $[Cr(CNC_6H_{11})_4(dppe)](PF_6)_2$ can be converted to a seven-coordinate species, $[Cr(CNC_6H_{11})_5(dppe)](PF_6)_2$, upon stirring a small quantity of this complex with neat cyclohexyl isocyanide. The spectroscopic and electrochemical properties of this complex were strikingly similar to those of $[Cr(CNC(CH_3)_3)_5(dppe)](PF_6)_2$ (section E).

Physical Measurements. Infrared spectra of Nujol mulls were recorded in the region 4000–400 cm^{-1} with a Beckman IR-12 spectrophotometer. Solution infrared spectra in the region 2200–1800 cm^{-1} were taken in dichloromethane with use of a liquid cell with KBr windows. A Perkin-Elmer R32 spectrometer was used to obtain the ^1H NMR spectra. Samples were dissolved in deuterated solvents, and resonances were usually referenced internally to Me_4Si. The PE-R32 spectrometer was also used to obtain magnetic moments by using the Evans method.[15,16] Cyclic voltammetry experiments were performed with the setup described previously.[17] X-ray photoelectron spectra (XPS) were obtained on a Hewlett-Packard 5950A ESCA spectrometer.[18]

Results and Discussion

Although the fission of the Cr–Cr quadruple bonds of $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ and $Cr_2(mhp)_4$ by alkyl isocyanides has not in our hands proved to be a viable synthetic route to homoleptic alkyl isocyanide complexes of chromium, we have found that the crystalline complexes $[Cr(CNR)_6](PF_6)_2$, where R = CMe_3 or C_6H_{11}, can be prepared conveniently and in good yield (50–75%) by an alternative route. The mixing of ethanolic solutions of chromium(II)[14] with an excess of the appropriate alkyl isocyanide and KPF_6 leads to the crystallization of the bright yellow complexes. If these six-coordinate species are treated with *neat* alkyl isocyanide or very concentrated chromium(II) solutions are mixed with an excess of RNC and KPF_6, then the corresponding seven-coordinate complexes $[Cr(CNR)_7](PF_6)_2$ are produced. This novel increase in coordination number from six to seven without a concomitant change in the metal oxidation state or the cation charge completes the first homologous series of homoleptic seven-coordinate complexes of any transition group (Cr, Mo,[4,19] and W[6,19,20]). Of further note is the fact that there is only one previous example of a homoleptic seven-coordinate complex of the first transition series. This is the vanadium(III) salt $K_4[V(CN)_7] \cdot 2H_2O$.[21]

The identity of $[Cr(CNR)_7](PF_6)_2$ as an authentic seven-coordinate species has been established by a crystal structure determination on the *tert*-butyl isocyanide derivative, full details of which will be reported elsewhere.[22] The geometry

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Table I. Infrared Spectra and Magnetic Moments of Alkyl Isocyanide Complexes of Chromium(II)

	$\nu(\mathrm{C{\equiv}N})$, cm^{-1}		
complex	NM[a]	CH_2Cl_2	μ_{obsd}, μ_B[b]
$[Cr(CNCMe_3)_6](PF_6)_2$	2180 s	2176 s	2.87
$[Cr(CNCMe_3)_7](PF_6)_2$	2160 s	*d*	*d*
$[Cr(CNC_6H_{11})_6](PF_6)_2$	2185 s	2184 s	2.75
$[Cr(CNC_6H_{11})_7](PF_6)_2$	2150 s	*d*	*d*
$[Cr(CNCMe_3)_4(PEt_3)_2](PF_6)_2$	2137 s	2126 s	2.60
$[Cr(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$	2133 s	2129 s	2.93
$[Cr(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)_2](PF_6)_2$	2128 s	2127 s	2.85
$[Cr(CNCMe_3)_4(dppe)](PF_6)_2$	2190 m s, 2154 s	2186 m, 2145 s	2.69
$[Cr(CNCMe_3)_5(dppe)](PF_6)_2$	2175 m, 2130 s, 2105 s, 2045 sh	*d*	*c*
$[Cr(CNC_6H_{11})_4(PEt_3)_2](PF_6)_2$	2146 s	2137 s	2.64
$[Cr(CNC_6H_{11})_4(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$	2148 s	2136 s	2.75
$[Cr(CNC_6H_{11})_4(P\text{-}n\text{-}Bu_3)_2](PF_6)_2$	2150 s	2137 s	2.73
$[Cr(CNC_6H_{11})_4(dppe)](PF_6)_2$	2197 m s, 2162 s	*c*	2.78
$[Cr(CNC_6H_{11})_5(dppe)](PF_6)_2$	2186 m s, 2131 s, br	*d*	*c*

[a] NM = Nujol mull. [b] Bohr magnetons; determined on dichloromethane solutions by the Evans method. [c] Not measured. [d] Solutions decompose–see text.

is very close to that of the 4:3 (C_s) piano stool while that of the related molybdenum(II)[23] and tungsten(II)[24] complexes is capped trigonal prismatic.

The room-temperature magnetic moment (Gouy method) of solid $[Cr(CNCMe_3)_6](PF_6)_2$ is 2.9 ± 0.1 μ_B, in accord with low-spin chromium(II), while $[Cr(CNCMe_3)_7](PF_6)_2$ was found to be diamagnetic. The Nujol mull infrared spectra of $[Cr(CNR)_6](PF_6)_2$ and $[Cr(CNR)_7](PF_6)_2$ were characterized by intense, reasonably sharp $\nu(\mathrm{C{\equiv}N})$ modes at ~2180 and ~2155 cm^{-1}, respectively (Table I). While dichloromethane solutions of $[Cr(CNR)_6](PF_6)_2$ also exhibit a single intense $\nu(\mathrm{C{\equiv}N})$ mode at frequencies similar to those of the solids (Table I), it is clear from IR spectral measurements that dichloromethane solutions of $[Cr(CNR)_7](PF_6)_2$ decompose to the analogous six-coordinate species through dissociation of one of the isocyanide ligands. This process has also been monitored by means other than IR spectroscopy, namely, ^1H NMR spectroscopy, solution magnetic moment determinations, and, as discussed later, cyclic voltammetry.

In the case of the ^1H NMR spectrum of $[Cr(CNCMe_3)_7](PF_6)_2$, the complex initially exhibits a single sharp resonance in acetone-d_6 at 1.64 ppm relative to Me_4Si, a value which is comparable to those which have been reported for its molybdenum and tungsten analogues (δ 1.62 and 1.59, respectively, in $CDCl_3$).[19] This resonance decreases in intensity over a period of several minutes, and a new broad peak grows in at δ ~4.1, which is characteristic of authentic $[Cr(CNCMe_3)_6](PF_6)_2$. The cyclohexyl resonances at δ ~4.35 and ~1.50 in the ^1H NMR spectrum of the diamagnetic seven-coordinate complex (data recorded from δ +10 to 0 in acetone-d_6) collapse and new broad resonances at δ 5.4, 3.25, and 1.4 emerge as the paramagnetic complex $[Cr(CNC_6H_{11})_6](PF_6)_2$ is formed. Careful studies of the ^1H NMR spectra of CD_2Cl_2 solutions of the pure six-coordinate complex (from δ +10 to −10) show that at 35 °C it is actually characterized by five resonances of comparable intensity, at δ 5.65, 4.35, 3.1, 1.5, and −3.8.[25]

A further reflection of this coordination number change is seen in the magnetic properties of dichloromethane solutions of $[Cr(CNR)_7](PF_6)_2$ and $[Cr(CNR)_6](PF_6)_2$. The magnetic moments of solutions of the six-coordinate species were determined (by the Evans method)[15] to be ~2.8 μ_B (Table I), in accord with their possessing a t_{2g}^4 ground-state configuration. While the diamagnetism of solid $[Cr(CNCMe_3)_7](PF_6)_2$ was confirmed by Gouy measurements, the magnetic moment of a dichloromethane solution was observed to be 2.82 μ_B within a few minutes of its preparation. In the case of $[Cr(CNC_6H_{11})_7](PF_6)_2$, we attempted to suppress this dissociation by dissolving the complex in a cyclohexyl isocyanide–benzene solution (19:1), but even here a small quantity of the six-coordinate species formed as evidenced by a measured magnetic moment of 0.74 μ_B. Apparently, the only solvent which suppresses dissociation completely is the neat alkyl isocyanide itself.

Substitution Chemistry: Reactions with Tertiary Phosphines. Both the six- and seven-coordinate homoleptic isocyanide cations react quite rapidly with the tertiary phosphines PR_3 (R = Et, *n*-Pr, or *n*-Bu) and with 1,2-bis(diphenylphosphino)ethane to form the six-coordinate mixed-ligand complexes $[Cr(CNR)_4(PR_3)_2](PF_6)_2$ and $[Cr(CNR)_4(dppe)](PF_6)_2$. These paramagnetic species (μ =. 2.6–2.9 μ_B for dichloromethane solutions; see Table I) were characterized by IR spectroscopy and cyclic voltammetry (vide infra). The complexes with monodentate phosphines $[Cr(CNR)_4(PR_3)_2](PF_6)_2$ exhibit a single $\nu(\mathrm{C{\equiv}N})$ in both Nujol mulls and dichloromethane (Table I), an observation which is in accord with a *trans*-$[Cr(CNR)_4(PR_3)_2]^{2+}$ geometry. As expected, the six-coordinate dppe derivatives have more complex IR spectra in the $\nu(\mathrm{C{\equiv}N})$ region (Table I). This supports their possessing a cis geometry. The $\nu(\mathrm{C{\equiv}N})$ modes in the $[Cr(CNR)_4(PR_3)_2](PF_6)_2$ compounds are ~40 cm^{-1} lower in energy compared to their homoleptic analogues $[Cr(CNR)_6](PF_6)_2$. This most likely reflects the increased σ-donor strength of phosphines, as well as their less effective π-accepting ability, as compared to the isocyanide ligands.

While the molybdenum and tungsten cations $[M(CNR)_7]^{2+}$ also undergo substitution reactions with phosphine ligands (up to two RNC ligands can be replaced by phosphines),[5,6] they differ from the corresponding reactions of $[Cr(CNR)_7]^{2+}$ in that they are not accompanied by a decrease in coordination number from seven to six. However, like the conversion of $[Cr(CNR)_6](PF_6)_2$ to $[Cr(CNR)_7](PF_6)_2$ by neat RNC (vide supra), we find that the same treatment of $[Cr(CNR)_4(dppe)](PF_6)_2$ with RNC affords $[Cr(CNR)_5(dppe)](PF_6)_2$. The dissolution of the latter seven-coordinate complexes in solvents such as dichloromethane leads to the reversal of this process via the loss of an isocyanide ligand.

Electrochemical Properties. These properties of the six- and seven-coordinate homoleptic and mixed-ligand complexes were

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[25] As the temperature is lowered in increments down to −35 °C, the resonances at δ 5.65, 4.35, and 3.1 broaden and finally collapse and that at δ 1.5 remains relatively unaffected while the upfield resonance at δ −3.8 shifts to δ −5.0. (These chemical shifts are referenced to a CD_2Cl_2 solvent impurity at δ 5.35.) Further studies of these temperature-dependent ^1H NMR spectra are planned.

Table II. Voltammetric Half-Wave Potentials for Alkyl Isocyanide Complexes of Chromium(II)[a]

complex	$E_{1/2}$(Ox)[b]	$E_{1/2}$(Red)(1)[b]	$E_{1/2}$(Red)(2)[b]
$[Cr(CNCMe_3)_6](PF_6)_2$	+0.84 (80)	−0.28 (140)	−1.04 (90)
$[Cr(CNCMe_3)_7](PF_6)_2$	+1.12[c]		
$[Cr(CNC_6H_{11})_6](PF_6)_2$	+0.75 (110)	−0.31 (80)	−1.08 (100)
$[Cr(CNC_6H_{11})_7](PF_6)_2$	+1.15[c]		
$[Cr(CNCMe_3)_4(PEt_3)_2](PF_6)_2$	+0.67 (150)	−0.43 (130)	−1.37 (130)
$[Cr(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$	+0.66[c]	−0.43 (90)	−1.38 (80)
$[Cr(CNCMe_3)_4(P\text{-}n\text{-}Bu_3)_2](PF_6)_2$	+0.62 (120)	−0.44 (100)	−1.42 (90)
$[Cr(CNCMe_3)_4(dppe)](PF_6)_2$	+0.66 (100)	−0.23 (110)	−1.04 (70)
$[Cr(CNCMe_3)_5(dppe)](PF_6)_2$	+1.02[c]	−1.42[d]	
$[Cr(CNC_6H_{11})_4(PEt_3)_2](PF_6)_2$	+0.51 (90)	−0.50 (85)	−1.33 (90)
$[Cr(CNC_6H_{11})_4(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$	+0.52 (130)	−0.47 (90)	−1.31 (87)
$[Cr(CNC_6H_{11})_4(P\text{-}n\text{-}Bu_3)_2](PF_6)_2$	+0.52 (130)	−0.47 (90)	−1.32 (90)
$[Cr(CNC_6H_{11})_4(dppe)](PF_6)_2$	+0.63 (105)	−0.27 (95)	−1.05 (75)
$[Cr(CNC_6H_{11})_5(dppe)](PF_6)_2$	+1.00[c]	−1.45[d]	

[a] In volts vs. SCE with a Pt-bead electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Values of $E_{pa} - E_{pc}$ (in mV) at a sweep rate of 200 mV/s are given in parentheses. [c] E_{pa} value. [d] E_{pc} value.

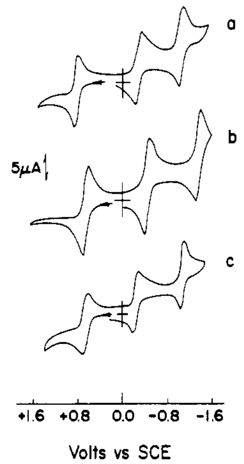

Figure 1. Cyclic voltammograms in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane of (a) $[Cr(CNCMe_3)_6](PF_6)_2$, (b) $[Cr(CNCMe_3)_4(PEt_3)_2](PF_6)_2$, and (c) $[Cr(CNCMe_3)_4(dppe)](PF_6)_2$. These were all recorded at 200 mV/s.

investigated with the cyclic voltammetry technique. Voltammetric half-wave potentials vs. SCE for 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane solutions are presented in Table II. In all instances the six-coordinate complexes exhibit a one-electron oxidation and two one-electron reductions (Table II and Figure 1).[26] For sweep rates (v) between 100 and 300 mV/s, $i_{pa}/i_{pc} \simeq 1$ and the ratio $i_p/v^{1/2}$ was constant in accord with diffusion control. The potential separation between the anodic and cathodic peaks, ΔE_p, was greater than 60 mV, being in the range 70–150 mV for a sweep rate of 200 mV/s. As we have discussed elsewhere,[27] these properties are (with our cell configuration) consistent with electron-transfer processes which are reversible or approach reversibility.

Exhaustive electrolyses were performed on dichloromethane solutions of several representative complexes by using potentials appropriate for the formation of chromium(III) or chromium(I) species. However, cyclic voltammograms of the resultant solutions indicated that significant levels of decomposition had occurred so we have not at this time pursued these studies further.

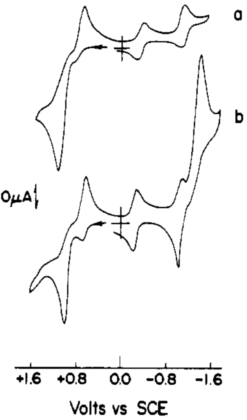

Figure 2. Cyclic voltammograms in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane of (a) $[Cr(CNC_6H_{11})_7](PF_6)_2$ and (b) $[Cr(CNCMe_3)_5(dppe)](PF_6)_2$. Both were recorded at 200 mV/s.

Of the mixed isocyanide–phosphine complexes listed in Table II, only $[Cr(CNCMe_3)_4(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$ exhibited a redox process which was clearly electrochemically irreversible. The oxidation $Cr^{2+} \rightarrow Cr^{3+}$ at E_{pa} = +0.66 V was coupled to a reduction wave at $E_{pc} \simeq +0.55$ V but with $i_{pc}/i_{pa} \ll 1$. Following this oxidation to Cr^{3+} and the subsequent reduction back to Cr^{2+}, the cathodic sweep showed a wave at −0.45 V, i.e., in the neighborhood of the reduction $Cr^{2+} \rightarrow Cr^{+}$, with a tremendously enhanced i_p. This is characteristic of adsorption occurring at the electrode following this irreversible process. After the cyclic voltammogram was recorded with a switching potential of +0.4 V for the anodic sweep, i.e., cathodic of the oxidation $Cr^{2+} \rightarrow Cr^{3+}$, then this adsorption phenomenon was not observed, and for the couple at $E_{1/2}$ = −0.43 V (Table II) the i_{pc}/i_{pa} ratio was equal to unity.

In comparing the voltammetric half-wave potentials of $[Cr(CNR)_6](PF_6)_2$ with those of their phosphine-substituted derivatives, we see that the $E_{1/2}$ values for the latter species are shifted to more negative potentials. This reflects the increased ability of phosphines to stabilize the chromium(III) oxidation state and their decreased effectiveness, relative to the RNC ligands, at stabilizing chromium(I) and chromium(0). This is an additional reflection of the greater σ-donor ability and/or poorer π-acceptor ability of PR_3 compared to RNC when bound to chromium. In making these comparisons we also note that the $E_{1/2}$ values for the *tert*-butyl isocyanide derivatives are in all instances at more positive potentials than their cyclohexyl isocyanide analogues.

In the case of the seven-coordinate species $[Cr(CNR)_7](PF_6)_2$ and $[Cr(CNR)_5(dppe)](PF_6)_2$, R = CMe_3 or C_6H_{11}, their cyclic voltammograms each reveal an irreversible oxi-

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(26) Determination of n values for representative complexes (n is the total number of equivalents of electrons transferred in exhaustive electrolyses at constant potentials) confirmed that these were one-electron processes (n = 1.0 ± 0.1). For example, n = 0.97 for the oxidation (at +1.0 V) of $[Cr(CNC_6H_{11})_6](PF_6)_2$, while for $[Cr(CNC_6H_{11})_4(dppe)](PF_6)_2$ oxidation at +1.0 V gave n = 0.87 while for reduction at −0.6 V, n = 1.11.

(27) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

dation in the range +1.0 to +1.15 V (E_{pa} values are listed in Table II). The coupled reduction wave was cathodic of the oxidation by ~400 mV (i.e., $E_{pa} - E_{pc} \simeq 400$ mV) and the ratio i_{pc}/i_{pa} was much less than unity. It was also apparent from these cyclic voltammograms (Figure 2) that appreciable quantities of the related six-coordinate species were present in these solutions. The origin of the latter seems to be twofold: first, that which is formed by ligand (RNC) loss from $[Cr(CNR)_7](PF_6)_2$ and $[Cr(CNR)_5(dppe)](PF_6)_2$ following their dissolution in the 0.2 M Bu_4NPF_6–CH_2Cl_2 solvent and, second, that formed by the same type of ligand loss following the irreversible electrochemical oxidation to $[Cr(CNR)_7]^{3+}$ and $[Cr(CNR)_5(dppe)]^{3+}$, i.e., by a coupled electrochemical–chemical mechanism. We are unable to determine the relative magnitudes of these two ligand loss mechanisms other than to note that the former, i.e., loss of RNC from the chromium(II) ions, is the more dominant of the two processes (as measured by peak currents).

The decomposition of $[Cr(CNR)_7]^{3+}$ following its electrochemical generation contrasts with the much greater stability of the analogous molybdenum and tungsten species.[6] Solutions of the $[Mo(CNR)_7]^{3+}$ and $[W(CNR)_7]^{3+}$ cations have been generated electrolytically in this same solvent system (0.2 M Bu_4NPF_6–CH_2Cl_2) and decompose at much slower rates.[28] A comparison between the electrochemical properties of Cr, Mo,[5] and W[5,6] complexes of the type $[M(CNR)_5(dppe)](PF_6)_2$ shows that $[Cr(CNR)_5(dppe)](PF_6)_2$ is irreversibly oxidized at potentials slightly less positive than those for the reversible oxidation of the molybdenum ($E_{1/2} = +1.18$ V for R = CMe_3 and +1.12 V for R = C_6H_{11})[5] and tungsten ($E_{1/2} = +1.07$ V for R = CMe_3)[6] analogues. Additionally, the chromium complexes exhibit an irreversible reduction ($E_{pc} \approx -1.45$ V)[29] which has no counterpart in the cyclic voltammograms of $[Mo(CNR)_5(dppe)](PF_6)_2$ and $[W(CNR)_5(dppe)](PF_6)_2$ within the solvent limits (+1.6 to −1.6 V) of the measurements. This difference correlates both with the ease of ligand loss from the Cr system and the greater accessibility of the reduction from chromium(II) to chromium(0) (to give the 18-electron species $[Cr(CNR)_4(dppe)]$) than is the case with the corresponding reductions of the second and third transition series elements Mo and W.

Comparisons with Aryl Isocyanide Complexes of Chromium and Related Systems. At the time we commenced the present study, there existed an interesting dichotomy in the chemistry of the isoelectronic homoleptic isocyanide and carbonyl complexes of the group 6 elements. While aryl isocyanides (ArNC) were known to form the six-coordinate monomers $M(CNAr)_6$,[7,9] which in the case of M = Cr could be oxidized both chemically and electrochemically to the mono- and dications $[Cr(CNAr)_6]^{n+}$,[30,31] the alkyl isocyanides (RNC) were, with the exception of $Cr(CNR)_6$,[32,33] known to form only the seven-coordinate 18-electron cations $[M(CNR)_7]^{2+}$, and then only for M = Mo and W.[4,6,19] The ability of ArNC to stabilize the lower oxidation states can be supported on experimental and theoretical grounds in terms of their greater π-acceptor ability compared to RNC.[9,31,34,35] However, it seemed to us that this difference was not necessarily sufficient to preclude the formation of the $[M(CNAr)_7]^{2+}$ and/or $[M(CNR)_6]^{n+}$ (n = 0–2) species, the isolation of which would afford an opportunity to compare directly the properties of analogous pairs of isoelectronic homoleptic alkyl and aryl isocyanide complexes of these elements. We have recently succeeded in preparing and characterizing the phenyl isocyanide complexes $[M(CNPh)_7](PF_6)_2$, where M = Mo or W,[10] and we have now demonstrated that $[Cr(CNR)_7](PF_6)_2$ and $[Cr(CNR)_6](PF_6)_2$ can be isolated in stable form in the crystalline state. In other words, we have established that these two important groups of "missing" complexes are readily obtained and that differences between the ArNC and RNC ligands do not appear to be sufficient to prevent the isolation of stable representative members of the pairs $M(CNR)_6$–$M(CNAr)_6$, $[M(CNR)_6]^{2+}$–$[M(CNAr)_6]^{2+}$, and $[M(CNR)_7]^{2+}$–$[M(CNAr)_7]^{2+}$ for M = Cr, Mo, or W.

One comparison which we have not made previously is that between the voltammetric half-wave potentials for $[Cr(CNR)_6](PF_6)_2$ (Table II) and the analogous potentials for $[Cr(CNPh)_6](PF_6)_2$, the latter occurring at +1.00, +0.25, and −0.35 V vs. SCE.[30] This permits a direct measure of the differences in thermodynamic stabilities of various oxidation states of $[Cr(CNR)_6]^{n+}$ and $[Cr(CNPh)_6]^{n+}$ and hence their relative accessibilities. The oxidation of $Cr^{2+} \rightarrow Cr^{3+}$ is more favored in the alkyl derivatives while the reductions $Cr^{2+} \rightarrow Cr^+$ and $Cr^+ \rightarrow Cr^0$ are clearly less favored. This greater accessibility of lower oxidation states in the aryl derivatives is by no means unexpected, as the greater π-acceptor ability of the aryl isocyanide ligands[9,31,34,35] should lead to a stabilization of the lower oxidation states. This seems to explain in a qualitative way why the reactions of aryl isocyanides with $M_2(O_2CCH_3)_4$ (M = Cr or Mo), $W_2(dmhp)_4$, and ethanolic solutions of chromium(II) afford[7,9,10] the stable zerovalent complexes $M(CNAr)_6$, while the less strongly reducing alkyl isocyanides favor[4–6] the retention of these metals in the divalent state, either as $[M(CNR)_6]^{2+}$ or $[M(CNR)_7]^{2+}$.

A final point to be addressed which relates to the difference in properties of $[Cr(CNR)_6]^{2+}$ vs. $[Cr(CNAr)_6]^{2+}$ concerns the results of X-ray photoelectron spectroscopic measurements (XPS). The Cr $2p_{3/2}$ binding energies of $[Cr(CNR)_6](PF_6)_2$, R = CMe_3 or C_6H_{11}, are significantly higher than those measured for the phenyl isocyanide species $[Cr(CNPh)_6]^+$ and $Cr(CNPh)_6$ (576.7, 575.3, and 574.5 eV, respectively). This smooth increase of E(Cr $2p_{3/2}$) with increase in oxidation state implies that neither Cr(d) to π^*(CNR) nor Cr(d) to π^*(CNAr) back-bonding is particularly dominant in influencing the charge at the metal center. If PhNC was a much better π-acceptor ligand than RNC, Cr(d) to π^*(CNPh) back-bonding in $Cr(CNPh)_6$ and $[Cr(CNPh)_6]^+$ might well be expected to increase the Cr 2p binding energies to a point where they approach those of $[Cr(CNR)_6]^{2+}$. Since we do not observe this, it can be argued that π-back-bonding differences between $[Cr(CNR)_6]^{n+}$ and $[Cr(CNAr)_6]^{n+}$ species are relatively small, and while these differences may be important they are insufficient to destabilize either set of complexes.

Acknowledgment. We thank the National Science Foundation (Grant CHE79-09233) for research support.

Registry No. $[Cr(CNC(CH_3)_3)_6](PF_6)_2$, 75215-52-0; $[Cr(CNC(CH_3)_3)_7](PF_6)_2$, 75215-56-4; $[Cr(CNC_6H_{11})_6](PF_6)_2$, 80083-26-7;

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(28) These molybdenum(III) and tungsten(III) cations are quite stable to decomposition to $[M(CNR)_6]^{3+}$. The dominant decomposition pathway in the electrochemical cell is reaction with chloride ion which diffuses from the auxiliary electrode compartment to the working electrode. This leads to the slow formation of $[M(CNR)_6Cl]^{2+}$. (Bell, A.; Klendworth, D. D.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 4456.)

(29) Peak currents suggest that this probably corresponds to a two-electron process.

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(32) Kündig, R. P.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1980**, 991 and references therein. Although the synthesis and spectroscopic characterizations of $Cr(CNR)_6$ have been described, little is yet known concerning their reactivity although these complexes are very sensitive to oxidation.

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$[Cr(CNC_6H_{11})_7](PF_6)_2$, 80083-28-9; $[Cr(CNC(CH_3)_3)_4(P(C_2H_5)_3)_2](PF_6)_2$, 80083-32-5; $[Cr(CNC(CH_3)_3)_4(P(C_3H_7)_3)_2](PF_6)_2$, 80063-24-7; $[Cr(CNC(CH_3)_3)_4(P(C_4H_9)_3)_2](PF_6)_2$, 80063-26-9; $[Cr(CNC(CH_3)_3)_4(dppe)](PF_6)_2$, 80063-28-1; $[Cr(CNC(CH_3)_3)_5(dppe)](PF_6)_2$, 80083-34-7; $[Cr(CNC_6H_{11})_4(P(C_2H_5)_3)_2](PF_6)_2$, 80063-30-5; $[Cr(CNC_6H_{11})_4(P(C_3H_7)_3)_2](PF_6)_2$, 80063-32-7; $[Cr(CNC_6H_{11})_4(P(C_4H_9)_3)_2](PF_6)_2$, 80083-36-9; $[Cr(CNC_6H_{11})_4(dppe)](PF_6)_2$, 80063-34-9; $[Cr(CNC_6H_{11})_5(dppe)](PF_6)_2$, 80106-37-2.

Contribution from the Departments of Organic Chemistry and Structural Chemistry,
The Weizmann Institute of Science, Rehovot, Israel

Hexagonal Structural Modification of $[Rh(dicbp)_2{}^+Cl^-]_n$ and Two-Dimensional $[Ir(dic)_2{}^+Cl^-]_n$ Polymers

AVI EFRATY,* IRENE FEINSTEIN, and FELIX FROLOW

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The preparation and characterization of a hexagonal structural modification of $[Rh(dicbp)_2{}^+Cl^-]_n$ (dicbp = 4,4′-diisocyanobiphenyl) is described: This stacked layer polymer contains an extensive network of columnar metal chains with intrachain Rh–Rh distances of 3.54 Å. The hexagonal polymer undergoes pressure-induced isomerization to the tetragonal structural modification. The preparation and characterization of a series of iridium polymers of the type $[Ir(dic)_2{}^+Cl^-]_n$ (dic = diisocyanide) are also described. The new iridium polymer consists of two-dimensional layered structures.

Introduction

Recently, we have reported the formation and characterization of coordination polymers of the type $[Rh(bridge)_2{}^+Cl^-]_n$ with stereochemically rigid diisocyanide linkages of different bridging geometries (e.g., collinear,[1] bent,[2] and parallel[3]). These rhodium(I) polymers consist of stacked layer tetragonal structures and contain extended networks of columnar metal chains.

The current study describes the formation and characterization of a hexagonal structural modification of $[Rh(dicbp)_2{}^+Cl^-]_n$, as well as certain two-dimensional diisocyanoiridium(I) polymers.

Experimental Section

Diisocyanides,[4] $[Rh(CO)_2Cl]_2$,[5] and $[IrCl(cod)]_2$[6] (cod = 1,5-cyclooctadiene) were prepared according to published procedures. Reactions were routinely carried out under argon atmosphere. Solvents used during the course of this investigation were dried, deoxygenated, and freshly distilled before being used. Microanalyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium, Mulheim, West Germany, as well as by the Microanalytical Laboratory at the Weizmann Institute.

Infrared spectra were recorded on a Perkin-Elmer 237 grating IR spectrometer and calibrated with the aid of a polystyrene film. Diffuse-reflectance spectra were measured on a Cary-15 spectrophotometer. Powder X-ray diffractometric traces were obtained on a Phillips diffractometer using filtered Cu radiation and a scan speed of 1° (2θ) min^{-1}.

$[Rh(dicbp)_2{}^+Cl^-]_n$ (Hexagonal Modification). A solution of 4,4′-diisocyanobiphenyl (0.79 g, 3.85 mmol) in CH_2Cl_2 (50 mL) was added at a steady rate of 0.3 mL min^{-1} into a magnetically stirred solution of $[Rh(CO)_2Cl]_2$ (0.15 g, 0.39 mmol) in the same solvent (50 mL) at ambient temperature (25 °C). The bright green polycrystalline polymer $[Rh(dicbp)_2{}^+Cl^-]_n$, formed in a quantitative yield (on the basis of the rhodium reactant), was filtered off, washed with CH_2Cl_2 (200 mL), and then vacuum-dried (80 °C (0.1 torr)). Anal. Calcd for $C_{28}H_{16}N_4ClRh$: C, 61.48; H, 2.93; N, 10.25; Cl, 6.49; Rh, 18.84. Found: C, 61.53; H, 3.35; N, 10.24; Cl, 5.99; Rh, 18.88. This polymer neither melts nor decomposes below 300 °C. The powder X-ray diffractometric trace data for this polymer are furnished in Table I.

Table I. Powder X-ray Diffraction Angles (θ, Deg), Interplanary Spacings (Å), Sin^2 θ Ratio Terms, and Assigned Indices for the New Hexagonal Polymer[a]

θ [$\theta_{calcd}{}^b$]	d	$N_{exptl}{}^c$ [$N_{theor}{}^d$]	assigned indices h	k	l
1.69 [1.69]	26.12	1 [1]	1	0	0
2.93 [2.92]	15.07	3.00 [3]	1	1	0
3.37 [3.38]	13.10	3.97 [4]	2	0	0
5.05 [5.07]	8.75	8.91 [9]	3	0	0
5.85 [5.86]	7.56	11.94 [12]	2	2	0
6.07 [6.10]	7.28	12.85 [13]	3	1	0
6.77 [6.77]	6.53	15.98 [16]	4	0	0
8.47 [8.48]	5.23	24.94 [25]	5	0	0
8.97 [8.98]	4.94	27.95 [28]	4	2	0
9.45 [9.45]	4.69	30.99 [31]	5	1	0
10.18 [10.19]	4.36	35.94 [36]	6	0	0
11.80 [11.78]	3.77	48.08 [48]	4	4	0
12.27 [12.28]	3.62	51.93 [52]	6	2	0
12.56 [12.57]	3.54	54.37[e]	0	0	1
12.71 [12.68]	3.50	55.66[e]	1	0	1
12.89 [12.91]	3.45	57.22[f]	1	1	1
12.89[g] [12.86]	3.45	57.22[f] [57]	7	1	0
13.02 [13.03]	3.42	58.36[e]	2	0	1
13.58 [13.58]	3.28	63.39[f]	3	0	1
13.58[g] [13.65]	3.28	63.39[f] [64]	8	0	0
14.29 [14.33]	3.12	70.05[e]	4	0	1
15.55 [15.53]	2.87	82.65[e]	4	2	1

[a] Space group $P6$: cell dimensions $a(=b) = 30.16$ Å, $c = 3.54$ Å. [b] Calculated from $\sin^2\theta(hkl) = A(h^2 + hk + k^2) + Cl^2$, where $A = \lambda^2/3a^2$ and $C = \lambda^2/4c^2$. [c] $N_{exptl} = \sin^2\theta(hk0)/\sin^2\theta(100)$. [d] $N_{theor} = h^2 + hk + k^2$. [e] Differs slightly from the nearest N_{theor} term. [g] And/or.

$[Ir(dic)_2{}^+Cl^-]_n$ Polymers. A general procedure for the preparation of the iridium polymers involves the dropwise addition of a CH_2Cl_2 solution (50 mL) of the diisocyanide (~1.0 mmol) into a magnetically stirred solution of $[IrCl(cod)]_2$ (0.15 g, 0.23 mmol) in the same solvent (25 mL) at ambient temperature (~25 °C). The gray-brown precipitates of the products formed during the course of these reactions were filtered off, extensively washed with CH_2Cl_2, and then vacuum-dried at 80 °C (0.1 torr). The new polymeric products, which were characterized as $[Ir(dic)_2{}^+Cl^-]_n$, are formed in a quantitative yield with respect to the starting iridium complex. The elemental compositional data of the iridium polymers are as follows. Anal. Calcd for the 1,4-diisocyanobenzene polymer ($C_{16}H_8N_4ClIr$): C, 39.70; H, 1.65; N, 11.58; Cl, 7.23; Ir, 39.74. Found: C, 39.80; H, 1.90; N, 11.34; Cl, 6.98; Ir, 39.92.

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