

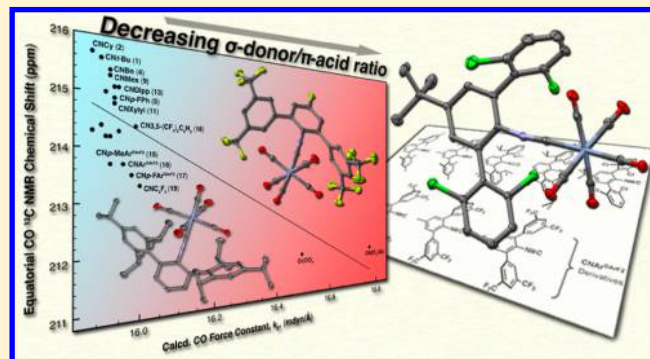
Comparative Measure of the Electronic Influence of Highly Substituted Aryl Isocyanides

Alex E. Carpenter, Charles C. Mokhtarzadeh, Donald S. Ripatti, Irena Havrylyuk, Ryo Kamezawa, Curtis E. Moore, Arnold. L. Rheingold, and Joshua S. Figueroa*

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, Mail Code 0358, La Jolla, California, 92093-0358, United States

S *Supporting Information*

ABSTRACT: To assess the relative electronic influence of highly substituted aryl isocyanides on transition metal centers, a series of C_{4v} -symmetric $Cr(CNR)(CO)_5$ complexes featuring various alkyl, aryl, and *m*-terphenyl substituents have been prepared. A correlation between carbonyl-ligand $^{13}C\{^1H\}$ NMR chemical shift (δ_{CO}) and calculated Cotton–Kraihanzel (C–K) force constant (k_{CO}) is presented for these complexes to determine the relative changes in isocyanide σ -donor/ π -acid ratio as a function of substituent identity and pattern. For nonfluorinated aryl isocyanides possessing alkyl or aryl substitution, minimal variation in effective σ -donor/ π -acid ratio is observed over the series. In addition, aryl isocyanides featuring strongly electron-releasing substituents display an electronic influence that nearly matches that of nonfluorinated alkyl isocyanides. Lower σ -donor/ π -acid ratios are displayed by polyfluorinated aryl isocyanide ligands. However, the degree of this attenuation relative to nonfluorinated aryl isocyanides is not substantial and significantly higher σ -donor/ π -acid ratios than CO are observed in all cases. Substituent patterns for polyfluorinated aryl isocyanides are identified that give rise to low relative σ -donor/ π -acid ratios but offer synthetic convenience for coordination chemistry applications. In order to expand the range of available substitution patterns for comparison, the syntheses of the new *m*-terphenyl isocyanides $CNAr^{Tripp2}$, $CNp-MeAr^{Mes2}$, $CNp-MeAr^{DArF2}$, and $CNp-FAr^{DArF2}$ are also reported ($Ar^{Tripp2} = 2,6-(2,4,6-(i-Pr)_3C_6H_2)_2C_6H_3$); $p-MeAr^{Mes2} = 2,6-(2,4,6-Me_3C_6H_2)_2-4-Me-C_6H_2$; $p-MeAr^{DArF2} = 2,6-(3,5-(CF_3)_2C_6H_3)_2-4-Me-C_6H_2$; $p-FAr^{DArF2} = 2,6-(3,5-(CF_3)_2C_6H_3)_2-4-F-C_6H_2$).



■ INTRODUCTION

The isolobal analogy between carbon monoxide (CO) and organoisocyanides (CNR) has long been recognized in coordination chemistry.^{1–7} In general, isocyanides have been used as surrogates to CO when more sterically encumbering, cylindrically symmetric π -acidic ligands are desired. However, there is substantial evidence available demonstrating that, while qualitatively isolobal, there are significant quantitative electronic differences present between CO and CNR as ligands.^{3,6–8} These differences stem from the attenuated “group” electronegativity of NR relative to O, which renders organoisocyanides both stronger σ -donors and weaker π -acids than CO. This greater σ -donor/ π -acid ratio has been used to justify the observed tendency of organoisocyanides to stabilize metal centers in higher formal oxidation states relative to CO.^{9–11}

Despite these fundamental differences, organoisocyanides allow for electronic and steric modulation in a manner inaccessible to CO. For electronic modulation, it has been well established that the σ -donor/ π -acid ratio of an organoisocyanide can be modified by changes in substituent pattern.^{2,12–15} Accordingly, it has been shown that the presence of electron withdrawing substituents can result in a diminished

σ -donor/ π -acid ratio,^{13,14,16–19} which therefore serves as a strategy to approach the electronic influence inherent to CO. Notably, however, a systematic quantification of the relative electronic influence of isocyanides as a function of substituent identity and pattern is only available for a small set of substituents.^{13,14,20,21} In addition, the limits of this approach, specifically in the context of the degree and type of substitution necessary for an organoisocyanide to fully mimic the electronic properties of CO, have not been clearly articulated.

Over the past several years, our group has explored the coordination chemistry of *m*-terphenyl isocyanides for use as isolobal surrogates to CO.^{22–35} This ligand class takes advantage of the encumbering steric properties of the *m*-terphenyl group^{36–44} as a means of generating coordinatively unsaturated isocyanide complexes that formally mimic the binary unsaturated metal carbonyls.^{45–48} Recently, we reported the synthesis of the fluorinated *m*-terphenyl isocyanide ligand CNAr^{DarF2} (Ar^{DarF2} = 2,6-(3,5-(CF₃)₂C₆H₃)₂C₆H₃).³³ Using zerovalent *mer*-Mo(CO)₃(CNR)₃ complexes as a coordination

Received: December 29, 2014

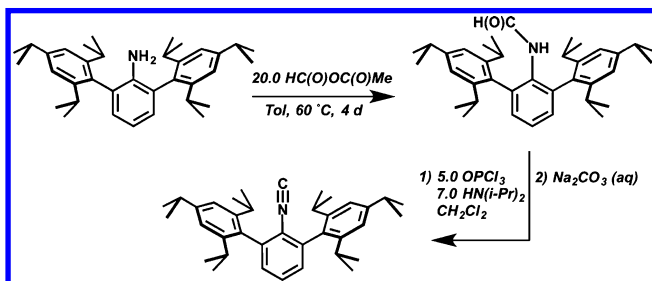
platform, we noted that $\text{CNAr}^{\text{DArF2}}$ gave rise to significantly blue-shifted ν_{CO} bands relative to the *m*-terphenyl isocyanide $\text{CNAr}^{\text{Mes2}}$ ($\text{Ar}^{\text{Mes2}} = 2,6-(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$),^{22,23} which features electron-releasing alkyl-substituted flanking rings. While only a crude estimate, this result indicated to us that $\text{CNAr}^{\text{DArF2}}$ possessed a lower σ -donor/ π -acid ratio than $\text{CNAr}^{\text{Mes2}}$, despite the fact that its flanking-ring CF_3 groups are quite distal from the isocyano unit. Given this observation, we became interested in systematically assessing the relative electronic influence of highly substituted *m*-terphenyl isocyanides on transition metal centers. Our aim was to identify both flanking-ring and backbone substitution patterns that either significantly alter the σ -donor/ π -acid ratio of the isocyano unit or exert a purely steric influence relative to less-substituted aryl isocyanide ligands. In addition, we aimed to understand the degree and type of substitution necessary for an isocyanide to most accurately mimic the electronic properties of CO.

Accordingly, in this report, we present a series of monoisocyanide $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes featuring an extensive range of alkyl, aryl, and *m*-terphenyl substitution patterns, including the new *m*-terphenyl derivatives $\text{CNAr}^{\text{Tripp2}}$, $\text{CNp-MeAr}^{\text{Mes2}}$, $\text{CNp-MeAr}^{\text{DArF2}}$, and $\text{CNp-FAr}^{\text{DArF2}}$ ($\text{Ar}^{\text{Tripp2}} = 2,6-(2,4,6-(i\text{-Pr})_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$; $p\text{-MeAr}^{\text{Mes2}} = 2,6-(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{-4-Me-C}_6\text{H}_2$; $p\text{-MeAr}^{\text{DArF2}} = 2,6-(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_2\text{-4-Me-C}_6\text{H}_2$; $p\text{-FAr}^{\text{DArF2}} = 2,6-(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_2\text{-4-F-C}_6\text{H}_2$). Using vibrational and NMR spectroscopy, we present a correlation between Cotton–Kraihanzel CO force constant (k_{CO})⁴⁹ and the ^{13}C chemical shift ($\delta_{^{13}\text{C}}$) that elucidates the electronic influence of each isocyanide in the series. Notably, $k_{\text{CO}}/\delta_{^{13}\text{C}}$ correlations have been used previously to provide insight into the electronic influence of coordinated phosphines, phosphites, and arsines,⁵⁰ as well as a few organoisocyanides.^{20,51} Our results indicate that substituent variation can alter the σ -donor/ π -acid ratio of an isocyanide ligand, but not to a significant extent. In addition, our data suggest that practical limitations exist for the use of isocyanides with σ -donor/ π -acid ratios matching that of CO.

RESULTS AND DISCUSSION

1. Synthesis of the *m*-Terphenyl Isocyanide Ligands $\text{CNAr}^{\text{Tripp2}}$, $\text{CNp-MeAr}^{\text{Mes2}}$, $\text{CNp-MeAr}^{\text{DArF2}}$, and $\text{CNp-FAr}^{\text{DArF2}}$. The synthetic routes to $\text{CNAr}^{\text{Tripp2}}$, $\text{CNp-MeAr}^{\text{Mes2}}$, $\text{CNp-MeAr}^{\text{DArF2}}$, and $\text{CNp-FAr}^{\text{DArF2}}$ are outlined in Schemes 1–3. Formylation of the known aniline, $\text{H}_2\text{NAr}^{\text{Tripp2}}$,⁵² with formylacetic anhydride provided the formamide, $\text{HC(O)N(H)Ar}^{\text{Tripp2}}$, which was subsequently dehydrated with $\text{OPCl}_3/\text{Na}_2\text{CO}_3$ to produce $\text{CNAr}^{\text{Tripp2}}$ as a colorless, nonvolatile solid in 95% isolated yield (Scheme 1). The IR spectra of $\text{CNAr}^{\text{Tripp2}}$ in the solid state (KBr) and C_6D_6 solution feature ν_{CN} bands at

Scheme 1



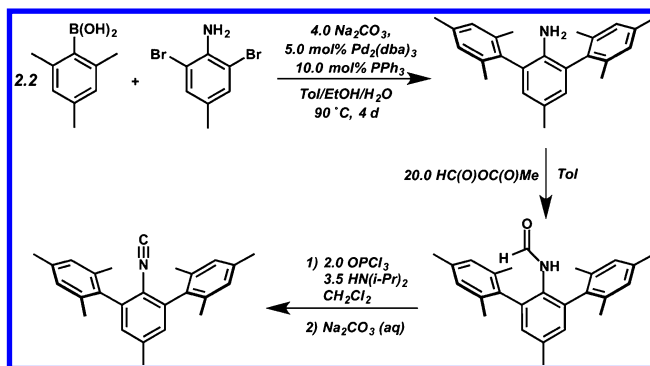
2114 and 2118 cm^{-1} , respectively. These spectroscopic signatures are similar to those found for $\text{CNAr}^{\text{Mes2}}$ and the 2,6-di-isopropylphenyl derivative $\text{CNAr}^{\text{Dipp2}}$ (Table 1; $\text{Ar}^{\text{Dipp2}} = 2,6-(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$).^{22,23}

Table 1. Infrared (Solution and Solid State) and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectroscopic Data for Free *m*-Terphenyl Isocyanides

compound	ν_{CN} (C_6D_6 , cm^{-1})	ν_{CN} (KBr, cm^{-1})	$\delta_{^{13}\text{C}}$ (C_6D_6 , ppm)
$\text{CNAr}^{\text{Mes2}}$	2118	2120	170.7
$\text{CNp-MeAr}^{\text{Mes2}}$	2118	2121	170.0
$\text{CNAr}^{\text{Dipp2}}$	2118	2124	171.9
$\text{CNAr}^{\text{Tripp2}}$	2118	2114	171.7
$\text{CNAr}^{\text{Clips2}}$	2119	2132	172.0
$\text{CNp-MeAr}^{\text{DArF2}}$	2118	2118	174.8
$\text{CNAr}^{\text{DArF2}}$	2112	2119	175.4
$\text{CNp-FAr}^{\text{DArF2}}$	2113	2118	175.1

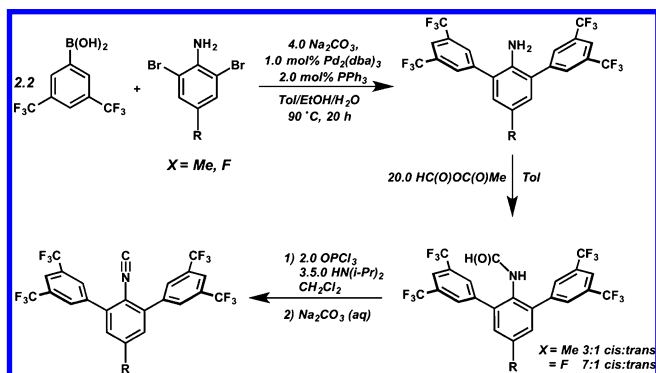
The *m*-terphenyl isocyanides $\text{CNp-MeAr}^{\text{Mes2}}$, $\text{CNp-MeAr}^{\text{DArF2}}$, and $\text{CNp-FAr}^{\text{DArF2}}$ were prepared by palladium-catalyzed cross coupling of *para*-substituted 2,6-dibromoanilines with either mesityl boronic acid or 3,5-bis-(trifluoromethyl)phenyl boronic acid, followed by formylation and dehydration (Schemes 2 and 3).⁵³ Whereas the cross-

Scheme 2



coupling step proceeded smoothly for the $p\text{-MeAr}^{\text{DArF2}}$ and $p\text{-FAr}^{\text{DArF2}}$ derivatives, construction of the sterically hindered $p\text{-MeAr}^{\text{Mes2}}$ framework required more forcing conditions and led to a low overall yield of $\text{CNp-MeAr}^{\text{Mes2}}$ (18%). The solution and solid-state IR spectra for $\text{CNp-MeAr}^{\text{Mes2}}$, $\text{CNp-MeAr}^{\text{DArF2}}$, and $\text{CNp-FAr}^{\text{DArF2}}$ all exhibit ν_{CN} bands between 2113 and

Scheme 3



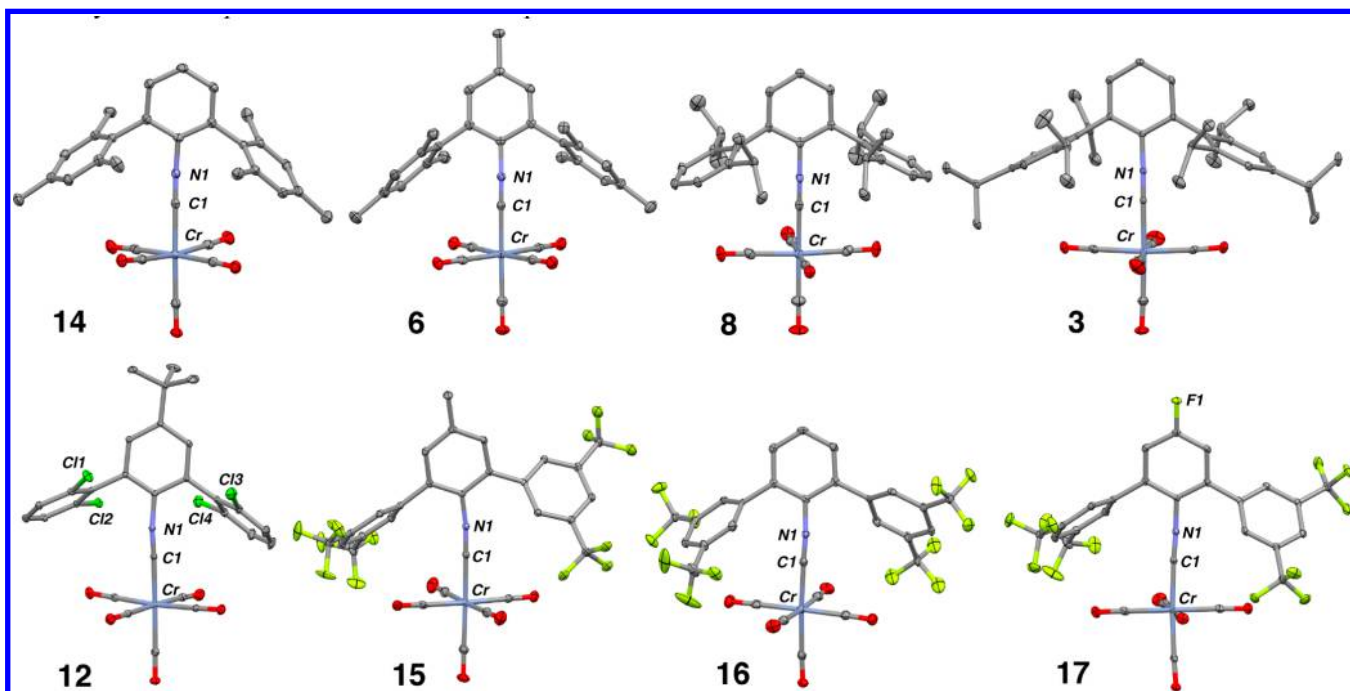


Figure 1. Molecular structures of *m*-terphenyl isocyanide $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes.

Table 2. Selected Bond Lengths for *m*-Terphenyl Isocyanide $\text{Cr}(\text{CNR})(\text{CO})_5$ Complexes

$\text{Cr}(\text{CNR}^{\text{R}2})(\text{CO})_5$	$d(\text{Cr}-\text{C}_{\text{iso}})$ (Å)	axial $d(\text{Cr}-\text{C}_{\text{CO}})$ (Å)	average equatorial $d(\text{Cr}-\text{C}_{\text{CO}})^a$ (Å)	$\text{CNR}^{\text{R}2}$ $d(\text{N}-\text{C}_{\text{ipso}})$ (Å)
$\text{Cr}(\text{CNAr}^{\text{Tripp}2})(\text{CO})_5$ (3)	1.968(2) ^b	1.902(2) ^b	1.904 (±0.009) ^b	1.396(2) ^b
$\text{Cr}(\text{CNp-MeAr}^{\text{Mes}2})(\text{CO})_5$ (6)	1.976(2)	1.885(2)	1.908 (±0.008)	1.399(2)
$\text{Cr}(\text{CNAr}^{\text{Dipp}2})(\text{CO})_5$ (8)	1.966(6)	1.874(6)	1.908 (±0.011)	1.392(6)
$\text{Cr}(\text{CNAr}^{\text{Clips}2})(\text{CO})_5$ (12)	1.974(2)	1.894(2)	1.910 (±0.009)	1.391(2)
$\text{Cr}(\text{CNAr}^{\text{Mes}2})(\text{CO})_5$ (14)	1.967(2)	1.894(2)	1.908 (±0.003)	1.395(2)
$\text{Cr}(\text{CNp-MeAr}^{\text{DArF}2})(\text{CO})_5$ (15)	1.970(2)	1.891(2)	1.911 (±0.010)	1.399(3)
$\text{Cr}(\text{CNAr}^{\text{DArF}2})(\text{CO})_5$ (16)	1.968(4)	1.895(5)	1.906 (±0.003)	1.395(5)
$\text{Cr}(\text{CNp-FAr}^{\text{DArF}2})(\text{CO})_5$ (17)	1.967(2)	1.894(2)	1.908 (±0.006)	1.397(2)

^aErrors reported as the standard deviation of the average equatorial $\text{Cr}-\text{C}_{\text{CO}}$ bond distances. ^bAverage of two crystallographically independent molecules.

2121 cm^{-1} , which is consistent with those observed for $\text{CNAr}^{\text{Mes}2}$ and $\text{CNAr}^{\text{DArF}2}$ (Table 1).

2. Synthesis and Molecular Structures of $\text{Cr}(\text{CNR})(\text{CO})_5$ Complexes. In order to directly compare the electronic influence of isocyanides over a range of substitution patterns, we sought a conveniently accessed coordination platform that featured (i) carbonyl ancillary ligands, (ii) a single isocyanide group, and (iii) well-defined IR and NMR spectroscopic signatures. These criteria stemmed from the established inverse-linear correlation between carbonyl ^{13}C chemical shift (δ) and CO force constant (k_{CO}) as a metal center becomes more effective at π -back-donation.^{20,50,51} In addition, the presence of a single isocyanide ligand was deemed necessary to isolate and quantify the effects of substitution pattern and identity. Accordingly, we targeted C_{4v} -symmetric $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes, which are known to meet these criteria.^{8,12,49,51}

The $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes 1–18 were prepared from the addition of CNR to photogenerated $\text{Cr}(\text{THF})(\text{CO})_5$ in THF solution and isolated in low to moderate yields (20–40%) by crystallization from *n*-pentane at -35°C . Complexes 1, 2, 4, 7, 10, 11, and 13, where $\text{R} = t\text{-Bu}$,^{8,54} cyclohexyl (Cy),⁵⁵ benzyl (Bn),⁵⁶ phenyl (Ph),⁵⁵ *p*-methylphenyl (*p*-MePh, i.e., tolyl),¹²

2,6-xylyl (Xyl),⁵⁷ and 2,6-*i*Pr)₂C₆H₃ (Dipp),⁵⁸ respectively, have been prepared previously by the same or other synthetic routes. Complexes 3, 6, 8, 12, and 14–17, which feature *m*-terphenyl isocyanides, were structurally characterized by X-ray diffraction (Figure 1). As shown in Table 2, substituent variation on either the central or flanking rings of the *m*-terphenyl framework has little effect on the $\text{Cr}-\text{C}$ bond lengths of the carbonyl ligands or isocyano unit. In addition, there is negligible change in the $\text{C}\equiv\text{N}$ or $\text{N}-\text{C}_{\text{ipso}}$ bond lengths as a function of substituent variation.

As we previously noted for $\text{CNAr}^{\text{DArF}2}$,³³ the presence of flanking 3,5-(CF₃)₂C₆H₃ rings on the *m*-terphenyl framework qualitatively presents the greatest steric encumbrance in the vicinity of the metal center. This is also the case for the new derivatives $\text{CNp-MeAr}^{\text{DArF}2}$ and $\text{CNp-FAr}^{\text{DArF}2}$ (Figure 1). For the parent $\text{CNAr}^{\text{DArF}2}$ ligand, this encumbrance resulted in significant steric pressures⁵⁹ that affected the isomeric preference of its $\text{Mo}(\text{CO})_3(\text{CNR})_3$ complexes relative to $\text{CNAr}^{\text{Mes}2}$ and $\text{CNAr}^{\text{Clips}2}$.³³ We believe these steric pressures are a consequence of the 3,5-disubstitution of the flanking *m*-terphenyl rings, which combine with the three-atom $\text{C}\equiv\text{N}-\text{C}$ linker to provide a more congested steric environment near the primary coordination sphere of a metal center. However, from a

Table 3. Carbonyl $^{13}\text{C}\{^1\text{H}\}$ NMR Chemical Shifts (δ , ppm; C_6D_6), Stretching Frequencies (ν , cm^{-1} ; C_6D_6), and Calculated C–K Force Constants (k_{m} , $\text{mdyn}/\text{\AA}$) for $\text{Cr}(\text{CNR})(\text{CO})_5$ Complexes 1–20 and $\text{Cr}(\text{CO})_6$ ^a

$\text{Cr}(\text{CNR})(\text{CO})_5$	axial CO ^{13}C NMR δ (ppm)	equatorial CO ^{13}C NMR δ (ppm)	$A_1^{(1)}$ (cm^{-1})	$A_1^{(2)}$ (cm^{-1})	B_1 (cm^{-1})	E (cm^{-1})	k_1 ($\text{mdyn}/\text{\AA}$)	k_2 ($\text{mdyn}/\text{\AA}$)	k_i ($\text{mdyn}/\text{\AA}$)
CN <i>t</i> -Bu (1)	217.6	215.6	2063	1950	1980	1950	15.54	15.91	0.28
CNCy (2)	217.6	215.7	2063	1948	1990	1948	15.55	15.89	0.28
CNAr ^{Tripp2} (3)	216.8	214.3	2056	1952	1996	1952	15.56	15.89	0.25
CNBn (4)	217.2	215.4	2064	1952	1993	1952	15.56	15.93	0.27
CN <i>p</i> -FPh (5)	216.7	214.9	2058	1956	1997	1956	15.56	15.94	0.25
CN <i>p</i> -MeAr ^{Mes2} (6)	217.2	214.4	2055	1954	1996	1954	15.58	15.91	0.25
CNPh (7)	216.8	215.0	2057	1954	1999	1954	15.59	15.92	0.25
CNAr ^{Dipp2} (8)	216.7	214.2	2055	1955	1995	1955	15.60	15.92	0.24
CN <i>Mes</i> (9)	217.3	215.3	2057	1955	1994	1955	15.60	15.93	0.25
CN <i>p</i> -MePh (10)	217.0	215.1	2058	1955	1997	1955	15.60	15.94	0.25
CNXyl (11)	216.7	214.8	2056	1956	1998	1956	15.61	15.94	0.24
CNAr ^{Clips2} (12)	216.8	214.2	2052	1957	1996	1957	15.62	15.93	0.23
CNDipp (13)	216.9	215.1	2057	1957	1996	1957	15.63	15.95	0.24
CNAr ^{Mes2} (14)	217.0	214.3	2054	1958	1999	1958	15.64	15.95	0.23
CN <i>p</i> -MeAr ^{DArF} (15)	215.4	213.7	2045	1960	2002	1960	15.65	15.93	0.21
CNAr ^{DArF2} (16)	215.2	213.7	2045	1963	2002	1963	15.69	15.96	0.20
CN <i>p</i> -FAr ^{DArF2} (17)	215.1	213.5	2044	1965	2003	1965	15.72	15.98	0.19
CN(3,5-(CF ₃) ₂ C ₆ H ₃) (18)	215.6	214.4	2046	1965	2002	1965	15.72	15.99	0.20
CNC ₆ F ₅ (19)	214.6 ^b	213.3 ^b	2041 ^c	1968 ^c		1968 ^c	15.76	16.00	0.18
CNCF ₃ (20)	211.5 ^d	211.7 ^d	2020 ^e	1950 ^e	2000 ^e	1950 ^e	16.36	16.77	0.31
	CO ^{13}C NMR δ (ppm)	A_{1g} (cm^{-1})	T_{1u} (cm^{-1})	E_g (cm^{-1})			k_2 ($\text{mdyn}/\text{\AA}$)	k_i ($\text{mdyn}/\text{\AA}$)	
$\text{Cr}(\text{CO})_6$	211.7	2100	1985	2020			16.49	0.22	

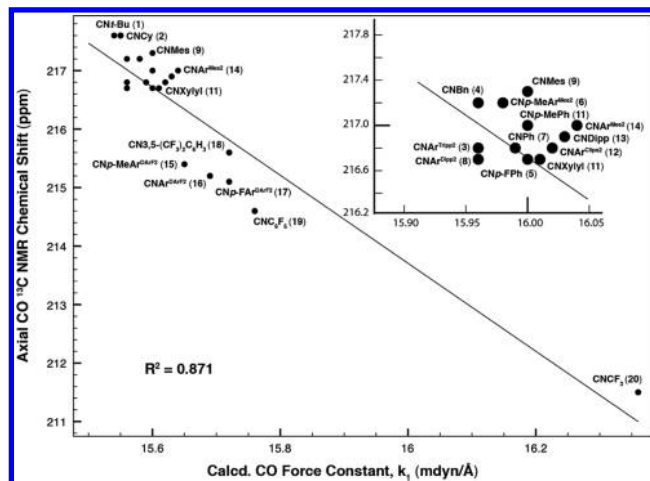
^aComplexes are listed by increasing k_1 value. ^bMeasured in CDCl_3 (ref 19). ^cMeasured in *n*-pentane (ref 19). ^dMeasured in CDCl_3 (ref 16).^eMeasured in the gas phase (ref 16).

qualitative perspective, CNAr^{Tripp2}, with its 4-*iso*-propyl group, also displays a significant degree of spatial extension near the Cr center in $\text{Cr}(\text{CNAr}^{\text{Tripp2}})(\text{CO})_5$ (3; Figure 1) in a manner absent for CNAr^{Mes2}, CN*p*-MeAr^{Mes2}, CNAr^{Dipp2}, and CNAr^{Clips2}. Accordingly, CNAr^{Tripp2} may be reasonably expected to exert significant steric pressures as a ligand in a manner rivaling the CNAr^{DArF} derivatives.

3. Correlation between the CO Force Constant (k_{CO}) and ^{13}C Chemical Shift (δ) for $\text{Cr}(\text{CNR})(\text{CO})_5$ Complexes.

As demonstrated by Gansow, the correlation between CO force constant and carbonyl ^{13}C chemical shift serves as a particularly good quantitative reporter of the electronic influence of coordinated ligands L in heteroleptic $\text{M}(\text{L})(\text{CO})_5$ complexes.⁵⁹ The correlation follows from the fact that CO force constants increase as π -backbonding from a metal center becomes less effective. Correspondingly, carbonyl ^{13}C chemical shifts show an upfield progression as the L ligand becomes an increasingly competitive π -acid.⁵¹ This latter effect is due to the dominance of the paramagnetic shielding term (σ) in determining the ^{13}C chemical shift of carbonyl ligands in strongly π -backbonding coordination environments.^{20,60,61}

The CO stretching frequencies, CO force constants (k_{CO}) calculated using the Cotton–Kraihanzel (C–K) approximation,^{49,62} and carbonyl $^{13}\text{C}\{^1\text{H}\}$ NMR data (δ_{C}) for complexes 1–18 are listed in Table 3. Plots of δ_{C} vs k_{CO} for the axial and equatorial CO ligands are shown in Figures 2 and 3, respectively. Also included are the data and calculated C–K force constants for Lentz's complexes $\text{Cr}(\text{CNC}_6\text{F}_5)(\text{CO})_5$ (19)¹⁹ and $\text{Cr}(\text{CNCF}_3)(\text{CO})_5$ (20),¹⁶ which feature the perfluorinated, but unencumbering, isocyanides CNC₆F₅ and CNCF₃, respectively. As shown in Figures 2 and 3, a reasonably good correlation between δ_{C} vs k_{CO} values is observed for both the axial and equatorial carbonyl ligands (corresponding to the

**Figure 2.** Carbonyl $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts (δ , ppm) versus calculated force constants for axial CO ligands (k_1 , $\text{mdyn}/\text{\AA}$) for $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes 1–20.

force constants k_1 and k_2 , respectively).⁴⁹ Ostensibly, the axial (k_1) and equatorial (k_2) CO force constants in these $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes report on different aspects of the isocyanide σ -donor/ π -acid ratio. While neither the σ -donor nor π -acid properties of an isocyanide can be completely isolated, the axial CO force constant is expected to be more sensitive to changes in σ -donor ability of a *trans*-CNR ligand, whereas the equatorial CO force constant (k_2) reports more fully on the combined isocyanide σ -donor/ π -acid properties. On this basis, several trends reflective of isocyanide electronic influence can be deduced from both Figures 2 and 3.

First, it is important to note that the relative spread of CO force constants (both k_1 and k_2) and ^{13}C chemical shifts is very

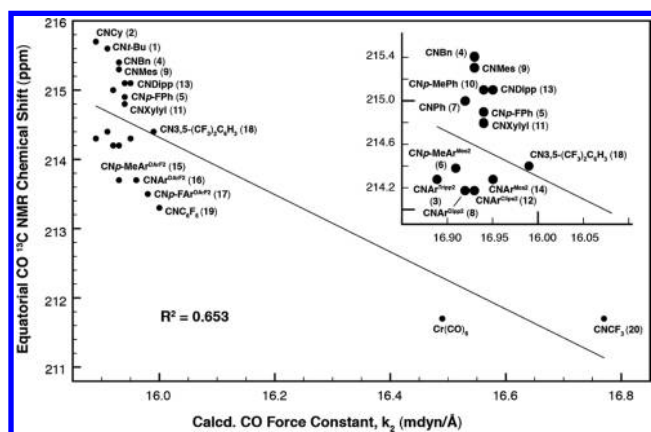


Figure 3. Carbonyl ^{13}C NMR chemical shifts (δ , ppm) versus calculated force constants for equatorial CO ligands (k_n , mdyne/Å) for $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes 1–20.

narrow over the series ($\Delta k_n \cong 1.0$ mdyne/Å; $\Delta \delta_C \cong 5$ ppm). Accordingly, in absolute terms, significant changes to both the ligand topology and substituent pattern do not have a dramatic effect on the electronic influence of a single isocyanide ligand. Second, while alkyl isocyanides can be interpreted as having the highest σ -donor/ π -acid ratio, as expected, this ratio is only marginally higher than that of monoaryl or polyaryl isocyanides featuring electron-releasing substituents. Indeed, as indicated by the δ_C vs k_n plots in Figures 2 and 3, the *m*-terphenyl isocyanide ligands $\text{CNAr}^{\text{Dipp}2}$ and $\text{CNAr}^{\text{Tripp}2}$, which are heavily substituted with electron-releasing *iso*-propyl groups in the flanking-ring positions, possess σ -donor/ π -acid ratios matching those of alkyl isocyanides.

Within the set of aryl isocyanides considered here, only polyfluorination leads to a measurable modulation of the isocyno σ -donor/ π -acid ratio. However, the degree of modulation is again not large. On the basis of the δ_C vs k_n plots in Figures 2 and 3, roughly two groupings of aryl isocyanides are apparent. One group consists of aryl isocyanides possessing electron releasing alkyl- or alkyl-substituted aryl groups, which all show nearly identical δ_C vs k_n values ($n = 1$ or 2) irrespective of substitution identity or pattern. The most notable comparison within this group is between the *m*-terphenyl isocyanide $\text{CNAr}^{\text{Mes}2}$ (in 14) introduced²² by our group and the commonly used aryl isocyanide CNXyl (in 11; $\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$).⁶³ On the basis of the δ_C vs k_n values of their complexes (Figures 2 and 3, insets), it is clear that the electronic influence of these two isocyanides is largely similar. Therefore, only differences in steric encumbrance should be expected to dictate their relative properties as ancillary ligands. In addition, it is noteworthy that the monofluorinated aryl isocyanide, $\text{CNp-FC}_6\text{H}_4$ (in 5), exhibits similar δ_C vs k_n values to those of nonfluorinated aryl isocyanides, thereby illustrating that a single fluoro substituent does not dramatically alter the σ -donor/ π -acid ratio of aryl isocyanides. A similar observation was made by Treichel when comparing the electrochemical properties of homoleptic $[\text{M}(\text{CNp-XC}_6\text{H}_4)_6]^n$ complexes ($\text{X} = \text{H, Me, F}$; $\text{M} = \text{Cr}$, $n = 0$; $\text{M} = \text{Mn}$, $n = 1+$).^{13,14}

The second group of aryl isocyanides is those featuring polyfluorinated substituents. As illustrated by the δ_C vs k_n values ($n = 1$ or 2), polyfluorination can be considered an effective means for lowering the σ -donor/ π -acid ratio of an aryl isocyanide. Furthermore, as indicated by Figure 2 (i.e., axial CO k_1 values), the lower isocyno σ -donor/ π -acid ratios found

for polyfluorinated aryl isocyanides may originate more significantly from an attenuation of σ -donor, rather an enhancement of π -acid, capability. However, relative to nonfluorinated aryl isocyanides, the magnitude of the change in σ -donor/ π -acid ratio upon polyfluorination is not substantial. This suggestion follows from the fact that CNC_6F_5 (in 19), which possesses the highest degree of fluorination proximal to the isocyno group, does not lead, in absolute terms, to significantly different δ_C vs k_n values than high σ -donor/ π -acid ratio aryl isocyanides (e.g., $\text{CNAr}^{\text{Tripp}2}$ (in 3) and $\text{CNAr}^{\text{Dipp}2}$ (in 8)). In addition and most importantly, the σ -donor/ π -acid ratio of CNC_6F_5 (in 19), as measured by δ_C vs k_2 (i.e., equatorial force constant; Figure 3),⁴⁹ is still significantly higher than that of CO,⁶⁴ despite substantial fluorination of the aryl backbone. This observation indicates that the aryl ring itself mitigates the ability to significantly control the σ -donor/ π -acid ratio of the isocyanide unit, especially for the goal of using substituent variation to achieve a σ -donor/ π -acid ratio rivaling CO. Accordingly, we contend that the δ_C vs k_n correlation shown in Figures 2 and 3 begins to define a lower limit for the ability of an aryl isocyanide to function as an electronic mimic of CO. Furthermore, as indicated from Figures 2 and 3, only polyfluorinated alkyl isocyanides, such as the difficult to prepare and handle derivative CNCF_3 (bp = -80°C),¹⁸ may be expected to display σ -donor/ π -acid ratios rivaling or exceeding that of CO.

Despite this important limitation of aryl isocyanides, it is noteworthy that fluorination of the aryl ring directly attached to the isocyno unit is not the only means of achieving relatively low σ -donor/ π -acid ratios. As indicated by Figures 2 and 3, distal fluorination of the type present in the *m*-terphenyl derivatives $\text{CNp-XAr}^{\text{DArF}2}$ ($\text{X} = \text{Me, H, F}$) can also effectively lower the σ -donor/ π -acid ratio of the isocyno unit relative to nonfluorinated aryl isocyanides. As the most extreme example, Figures 2 and 3 show that the *m*-terphenyl derivative $\text{CNp-FAr}^{\text{DArF}2}$ (in 17) gives rise to δ_C vs k_n values nearly matching those of CNC_6F_5 (in 19). Accordingly, the combination of distal, flanking-ring CF_3 groups and a single central-ring fluoro substituent can be viewed as equivalent to perfluorination in terms of its effect on the aryl isocyanide σ -donor/ π -acid ratio. Given that CNC_6F_5 is also difficult to prepare and spontaneously polymerizes when pure,^{18,65,66} we believe that distal-fluorination of an *m*-terphenyl or other polyaryl group⁶⁷ can therefore serve as an effective and more convenient strategy for obtaining aryl isocyanides with relatively low σ -donor/ π -acid ratios. However, it is likely that the σ -donor/ π -acid ratios of such polyfluorinated aryl isocyanides will remain substantially higher than that of CO.

CONCLUSIONS

In coordination chemistry, organoisocyanides have long been viewed as sterically and electronically tunable surrogates to carbon monoxide. While it has been recognized that organoisocyanides are both stronger σ -donors and less effective π -acids than CO, the extent of these differences has been less clearly established. This is particularly true for aryl isocyanides, where substituent modulation has been thought to afford control over the electronic influence of the isocyno unit. However, the results presented here for 20 different isocyanides demonstrate that the degree to which substituent variation can affect the electronic influence of an isocyno unit is substantially limited. For aryl isocyanides, the aryl group itself seemingly mitigates the ability of electron-withdrawing substituents to significantly

lower the effective σ -donor/ π -acid ratio of the isocyno unit. Furthermore, the presence of strongly electron-releasing substituents readily raises the σ -donor/ π -acid ratio of an aryl isocyanide ligand to values similar to alkyl isocyanides. The analysis presented here also suggests that σ -donor/ π -acid ratios matching or exceeding that of CO may only be achieved by perfluorinated alkyl isocyanides, which are known to be difficult to prepare and handle. However, distal polyfluorination, as in the $\text{CN}p\text{-XAr}^{\text{D}^{\text{ArF}_2}}$ derivatives presented here, can effectively lower the σ -donor/ π -acid ratio of an isocyno group in a synthetically and operationally convenient manner. Accordingly, we believe the results presented here will be useful for the design of transition-metal isocyanide complexes and contribute to a more detailed understanding of their electronic structure properties.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated according to standard procedures.⁶⁸ Unless otherwise stated, reagent-grade starting materials were purchased from commercial sources and purified by standard methods when necessary.⁶⁹ Benzene- d_6 (Cambridge Isotope Laboratories) was distilled from NaK/benzophenone and stored over 4 Å molecular sieves for 2 days prior to use. Chloroform- d (Cambridge Isotope Laboratories) was distilled from calcium hydride and stored over 4 Å molecular sieves for 2 days prior to use. The *m*-terphenyl aniline, $\text{H}_2\text{NAr}^{\text{Tripp}2}$,⁵² and isocyanides $\text{CNAr}^{\text{Mes}2}$, $\text{CNAr}^{\text{Dipp}2}$, $\text{CNAr}^{\text{D}^{\text{ArF}_2}}$, and $\text{CNAr}^{\text{Clips}2}$ were prepared according to published procedures.^{22,23,33} The isocyanides CN-*t*-Bu, CNCy, CN-*p*-PPh, CNPh, and CNBn (Cy = cyclohexyl; Bn = benzyl) were purchased from commercial sources and used as received. The isocyanides CNMes, CNXyl, and CN-*p*-Tol (Mes = 2,4,6-Me₃C₆H₂; Xyl = 2,6-Me₂C₆H₃; *p*-Tol = 4-MeC₆H₄) were prepared by formylation of the corresponding aniline with HC(O)OH in toluene, followed by dehydration with $\text{OPCl}_3/\text{NEt}_3/\text{Na}_2\text{CO}_3$ in CH_2Cl_2 . The known isocyanide $\text{CN}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)^{70}$ was prepared by the modified procedure described below. Full characterization data for $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes **1–18** are provided in the Supporting Information.

Solution ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Varian Mercury 300 and 400 spectrometers, a Varian X-Sens500 spectrometer, or a JEOL ECA-500 spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts are reported in ppm relative to SiMe_4 (^1H and ^{13}C , $\delta = 0.0$ ppm) with reference to residual solvent resonances of 7.16 ppm (^1H) and 128.06 ppm (^{13}C) for benzene- d_6 and 7.26 ppm (^1H) and 77.16 ppm (^{13}C) for chloroform- d .⁷¹ FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as C_6D_6 solutions injected into a ThermoFisher solution cell equipped with KBr windows or as KBr pellets. For solution FTIR spectra, solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to the sample. The following abbreviations were used for the intensities and characteristics of important IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, b = broad, vb = very broad, sh = shoulder. High-resolution mass spectrometry (HRMS) was performed using either an Agilent 6230 ESI-TOFMS instrument running in either positive or negative ion mode or a Thermo MAT900XL Electron Impact MS instrument running in negative ion mode. Combustion analyses were performed by Robertson Microlit Laboratories of Madison, NJ.

Synthesis of $\text{HC(O)NHA}^{\text{Tripp}2}$. Acetic anhydride (Ac_2O ; 17.7 g, 0.173 mol, 20 equiv) was cooled to 0 °C under a N_2 atmosphere and formic acid (7.96 g, 0.173 mol, 20 equiv) was added dropwise, via syringe, over 20 min. The mixture was stirred at 0 °C for 20 min and then heated to 50 °C for 5 h. The mixture, now containing formylacetic anhydride,⁷² was then cooled to room temperature and added, via cannula, to a THF solution of $\text{H}_2\text{NAr}^{\text{Tripp}2}$ (4.30 g, 8.65

mmol, 100 mL) over the course of 1 h. The reaction mixture was then heated to 60 °C for 4 days. Thereafter, the reaction mixture was allowed to cool to room temperature and the volatile components removed via rotary evaporation. The crude residue was then washed with H_2O (3×100 mL) to remove residual acetic acid. The resulting solid was then dissolved in Et_2O (200 mL), dried over MgSO_4 , and filtered. All volatile materials were then removed by rotary evaporation, and the resulting solid was suspended in EtOH (100 mL) and cooled to 0 °C. The mixture was then filtered to provide $\text{HC(O)NHA}^{\text{Tripp}2}$ as a colorless solid, which was dried *in vacuo*. Yield: 3.55 g, 6.76 mmol, 78.2%. ^1H NMR (400.1 MHz, CDCl_3 , 20 °C): δ = 7.66 (d, 1H, J = 11 Hz, HC(O)NH), 7.22 (t, 1H, *p*-Ph), 7.17 (d, 2H, J = 7 Hz, *m*-Ph), 7.087 (s, 4H, *m*-Tripp), 6.7 (br d, 1H, J = 11 Hz, HC(O)NH), 2.93 (septet, 2H, J = 7 Hz, *p*-($\text{CH}(\text{CH}_3)_2$)), 2.61 (septet, 4H, J = 7 Hz, *p*-($\text{CH}(\text{CH}_3)_2$)), 2.22 (br s, 2H, NH_2), 1.30 (d, 12 H, J = 7 Hz, ($\text{CH}(\text{CH}_3)_2$)), 1.12 (d, 12H, J = 7 Hz, ($\text{CH}(\text{CH}_3)_2$)), 1.10 (d, 12H, J = 7 Hz, ($\text{CH}(\text{CH}_3)_2$)) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 20 °C): δ = 162.8 (HC(O)N), 149.5, 146.4, 133.8, 132.4, 131.6, 131.0, 124.4, 121.9, 34.4 (($\text{CH}(\text{CH}_3)_2$)), 30.8 (($\text{CH}(\text{CH}_3)_2$)), 25.0 (($\text{CH}(\text{CH}_3)_2$)), 24.2 (($\text{CH}(\text{CH}_3)_2$)), 23.4 (($\text{CH}(\text{CH}_3)_2$)) ppm. FTIR (KBr window, CDCl_3): ν_{NH} = 3352 (w) cm^{-1} , ν_{CO} = 1677 (s) cm^{-1} , also 2964 (m), 2929 (w), 2870 (w), 1606 (w), 1461 (w), 1448 (w), 1410 (w), 1364 (w), 1318 (w), 1278 (w), 1070 (w) cm^{-1} . HRMS (ESI pos. ion; NCMe): m/z Calcd, 548.3863; m/z Found, 548.3864 [M]⁺.

Synthesis of $\text{CNAr}^{\text{Tripp}2}$. Diisopropyl amine ($\text{HN}(i\text{-Pr})_2$; 4.52 g, 44.63 mmol, 7 equiv) was added via syringe to a stirring CH_2Cl_2 solution of $\text{HC(O)NHA}^{\text{Tripp}2}$ (3.55 g, 6.38 mmol, 250 mL) under a N_2 atmosphere. The resulting mixture was cooled to 0 °C where POCl_3 (4.89 g, 31.9 mmol, 5 equiv) was added via syringe over 20 min. The resulting mixture was allowed to warm to room temperature and then stir for 12 h. Thereafter, aqueous Na_2CO_3 (1.5 M, 200 mL) was added and the reaction mixture was stirred for 1 h. The aqueous and organic layers were then separated and the aqueous layer washed with CH_2Cl_2 (3×100 mL). The combined organic extracts were then dried over MgSO_4 , filtered, and dried by rotary evaporation. The resulting residue was then suspended in NCMe (100 mL), filtered, washed with cold (0 °C) MeCN (2×25 mL), and dried *in vacuo* to afford $\text{CNAr}^{\text{Tripp}2}$ as a colorless solid. Yield: 3.07 g, 6.05 mmol, 94.8%. ^1H NMR (400.1 MHz, C_6D_6 , 20 °C): δ = 7.25 (s, 4H, *m*-Tripp), 7.02 (d, 2H, J = 7 Hz, *m*-Ph), 6.94 (t, 1H, J = 7 Hz, *p*-Ph), 2.86 (septet, 2H, J = 7 Hz, *p*-($\text{CH}(\text{CH}_3)_2$)), 2.78 (septet, 4H, J = 7 Hz, *o*-($\text{CH}(\text{CH}_3)_2$)), 1.37 (d, 12H, J = 7 Hz, ($\text{CH}(\text{CH}_3)_2$)), 1.24 (d, 12H, J = 7 Hz, ($\text{CH}(\text{CH}_3)_2$)), 1.18 (d, 12H, J = 7 Hz, ($\text{CH}(\text{CH}_3)_2$)) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6 , 20 °C): δ = 171.7 (CNR), 149.7, 146.7, 139.7, 132.9, 129.9, 128.5, 127.8, 121.4, 34.8 (($\text{CH}(\text{CH}_3)_2$)), 31.6 (($\text{CH}(\text{CH}_3)_2$)), 24.7 (($\text{CH}(\text{CH}_3)_2$)), 24.4 (($\text{CH}(\text{CH}_3)_2$)), 24.3 (($\text{CH}(\text{CH}_3)_2$)) ppm. FTIR (KBr window, C_6D_6): ν_{CN} = 2118 (s) cm^{-1} , also 2961 (m), 2930 (w), 2870 (w), 1464 (w), 1383 (w), 1363 (w), 1104 (w), 879 (w), 760 (w) cm^{-1} . FTIR (KBr pellet): ν_{CN} = 2114 (s) cm^{-1} , also 2962 (s), 2929 (s), 2904 (s), 2868 (s), 1666 (w), 1608 (m), 1570 (m), 1459 (s), 1422 (m, sh), 1380 (m), 1363 (m), 1316 (m), 1240 (m), 1105 (m), 1068 (m), 1054 (m), 1011 (w), 946 (m), 924 (w, sh), 876 (w, sh), 823 (m), 803 (m, sh), 757 (m), 652 (m) cm^{-1} . HRMS (ESI pos. ion; NCMe): m/z Calcd, 508.3938; m/z Found, 508.3941 [M]⁺.

Synthesis of $\text{H}_2\text{N}(p\text{-MeAr}^{\text{Mes}2})$. A resealable ampoule was charged with 2,6-dibromo-4-methylaniline (0.954 g, 3.60 mmol), mesityl boronic acid (MesB(OH)_2 ; 1.30 g, 7.92 mmol, 2.2 equiv), Na_2CO_3 (1.68 g, 15.84 mmol, 4.4 equiv), and toluene (30 mL). To this mixture was then added a toluene solution (10 mL) containing $\text{Pd}_2(\text{dba})_3$ (0.165 g, 0.18 mmol, 5 mol %; dba = dibenzylideneacetone), PPh_3 (0.094 g, 0.36 mmol, 10 mol %), followed by EtOH (10 mL) and H_2O (5 mL). The ampoule was sealed under an argon atmosphere and heated to 90 °C for 72 h. The resulting mixture was then cooled to room temperature and filtered through a medium porosity fritted funnel packed with Celite. Brine (50 mL) was added to the filtrate, and the resulting biphasic mixture was neutralized to pH \approx 7 using HCl (0.1 M). The aqueous and organic phases were then separated and the aqueous phase extracted with Et_2O (3×10 mL). The organic extracts were combined and dried over MgSO_4 . Volatile materials were then

removed by rotary evaporation and the resulting oil purified by column chromatography (silica gel) using hexanes to elute principle contaminants followed by a 0.5% EtOAc/hexanes solution to elute $\text{H}_2\text{N}(p\text{-MeAr}^{\text{Mes2}})$. Fractions containing $\text{H}_2\text{N}(p\text{-MeAr}^{\text{Mes2}})$ were combined and concentrated to a solid by rotary evaporation. Yield: 0.222 g, 0.648 mmol, 18.0%. ^1H NMR (499.8 MHz, C_6D_6 , 20 °C): δ = 6.91 (s, 4H, *m*-Mes), 6.75 (s, 2H, *m*-Ph), 2.91 (s, 2H, NH_2), 2.22 (s, 6H, *p*-Mes), 2.19 (s, 3H, *p*-MeAr), 2.17 (s, 12H, *o*-Mes) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6 , 20 °C): δ = 138.9, 137.1, 136.8, 136.1, 129.5, 128.9, 127.3, 126.4, 21.2 (*p*-MeAr), 20.8 (*p*-Mes), 20.4 (*o*-Mes) ppm. FTIR (C_6D_6 , KBr window): ν_{NH} = 3472 (m) and 3378 (m) cm^{-1} , also 3006 (m), 2970 (w), 2942 (w), 2915 (m), 2859 (w), 2713 (vw), 1610 (m), 1585 (m), 1480 (w), 1463 (s), 1377 (v), 1299 (vw), 1258 (m), 1097 (vw), 1036 (w), 1014 (w), 991 (vw), 866 (w), 852 (m), 775 (vw), 694 (vw) cm^{-1} . HRMS (ESI pos. ion; NCMe): m/z Calcd, 344.2373; m/z Found, 344.2372 [$\text{M}]^+$.

Synthesis of the *m*-Terphenyl Anilines $\text{H}_2\text{N}(p\text{-R}^{\text{DarF2}})$ (R = Me, F). A resealable ampoule was charged with the desired 2,6-dibromoaniline (3.60 mmol), 3,5-(CF_3) $_2\text{C}_6\text{H}_3\text{B}(\text{OH})_2$ (2.04 g, 7.92 mmol, 2.2 equiv), Na_2CO_3 (1.68 g, 15.84 mmol, 4.4 equiv), and toluene (30 mL). To this mixture was then added a toluene solution (10 mL) containing $\text{Pd}_2(\text{dba})_3$ (0.033 g, 0.036 mmol, 1 mol %; dba = dibenzylideneacetone), PPh_3 (0.019 g, 0.072 mmol, 2 mol %), followed by EtOH (10 mL) and H_2O (5 mL). The ampoule was sealed under an argon atmosphere and heated to 90 °C for 20 h. Work up and isolation was conducted in identical fashion to that of $\text{H}_2\text{N}(p\text{-MeAr}^{\text{Mes2}})$.

Data for $\text{H}_2\text{N}(p\text{-MeAr}^{\text{DarF2}})$. Yield: 0.860 g, 1.62 mmol, 45.0%. ^1H NMR (499.8 MHz, C_6D_6): δ = 7.76 (s, 2H, *p*-ArF), 7.70 (s, 4H, *o*-ArF), 6.50 (s, 2H, *m*-Ph), 2.59 (s, 2H, NH_2), 2.05 (s, 3H, *p*-MeAr) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6): δ = 142.1, 138.2, 132.5 (q, $^2J_{\text{CF}}$ = 33 Hz, *m*-ArF), 131.7, 129.7, 128.4, 125.3, 123.9 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3), 121.3 (septet, $^3J_{\text{CF}}$ = Hz, *p*-ArF), 20.2 (*p*-Me) ppm. ^{19}F NMR (282.3 MHz, C_6D_6 , 20 °C): δ = -63.31 (s, CF_3) ppm. FTIR (C_6D_6 , KBr window): ν_{NH} = 3459 (w) and 3378 (w) cm^{-1} , also 2959 (w), 2923 (m), 2854 (m), 1619 (m), 1480 (m), 1460 (w), 1363 (s), 1302 (m), 1277 (vs), 1183 (vs), 1141 (vs), 1105 (m), 899 (s), 841 (m), 811 (s), 708 (m), 680 (m), 641 (w) cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_{13}\text{F}_2\text{N}$: C, 52.00; H, 2.47; N, 2.64. Found: C, 50.83; H, 2.28; N, 2.64.

Data for $\text{H}_2\text{N}(p\text{-F}^{\text{DarF2}})$. Yield: 1.30 g, 2.43 mmol, 67.5%. ^1H NMR (499.8 MHz, C_6D_6): δ = 7.74 (s, 2H, *p*-ArF), 7.55 (s, 4H, *o*-ArF), 6.39 (d, 2H, $^2J_{\text{FH}}$ = 8 Hz, *m*-Ph), 2.45 (s, 2H, NH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6): δ = 156.3 (d, $^1J_{\text{CF}}$ = 239 Hz, *p*-Ph), 140.6, 136.9, 132.6 (q, $^2J_{\text{CF}}$ = 33 Hz, *m*-ArF), 129.5, 126.0 (d, $^3J_{\text{CF}}$ = 7 Hz, *o*-Ph), 123.7 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3), 121.8 (septet, $^3J_{\text{CF}}$ = 4 Hz, *p*-ArF), 117.7 (d, $^2J_{\text{CF}}$ = 20 Hz, *m*-Ph) ppm. ^{19}F NMR (282.3 MHz, C_6D_6 , 20 °C): δ = -63.33 (s, CF_3), -126.4 (t, $^2J_{\text{FH}}$ = 8 Hz, *p*-Ph) ppm. FTIR (C_6D_6 , KBr windows): 3478 (w), 3384 (w), 3081 (w), 1613 (vw), 1574 (s), 1465 (s), 1349 (s), 1274 (s), 1185 (s), 1141 (s), 1105 (s), 1074 (s), 916 (m), 889 (m) cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{10}\text{F}_3\text{N}$: C, 49.34; H, 1.89; N, 2.62. Found: C, 50.83; H, 2.28; N, 2.78.

Synthesis of the *m*-Terphenyl Formamides $\text{H}(\text{O})\text{CNH}(p\text{-R}'\text{Ar}^{\text{R2}})$ (R' = H, Me, F; R = Mes, DarF). Acetic anhydride (Ac_2O ; 5.9 g, 0.058 mol, 20 equiv) was cooled to 0 °C under a N_2 atmosphere, and formic acid (3.33 g, 0.073 mol, 25 equiv) was added dropwise, via syringe, over 10 min. The mixture was stirred at 0 °C for 20 min and then heated to 50 °C for 5 h. This mixture, now containing formyl acetic anhydride, was then cooled to room temperature and added, via syringe, to a toluene solution of $\text{H}_2\text{N}(p\text{-R}'\text{Ar}^{\text{R2}})$ (1.95 mmol). The resulting mixture was stirred for 16 h. Volatile materials were then removed by rotary evaporation to afford $\text{H}(\text{O})\text{CNH}(p\text{-R}'\text{Ar}^{\text{R2}})$ as a colorless solid, which was used without further purification.

Data for $\text{H}(\text{O})\text{CNH}(p\text{-MeAr}^{\text{Mes2}})$. Yield: 0.616 g, 1.66 mmol, 85%. ^1H NMR (499.8 MHz, CDCl_3 , 20 °C): δ = 7.59 (d, 1H, J = 12 Hz, $\text{HC}(\text{O})\text{NH}$), 6.94 (s, 6H, *m*-Mes and *m*-Ph), 6.49 (d, 1H, J = 12 Hz, $\text{HC}(\text{O})\text{NH}$), 2.37 (s, 3H, *p*-Ph), 2.31 (s, 6H, *p*-Mes), 2.01 (s, 12H, *o*-Mes) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 20 °C): δ = 162.8 ($\text{HC}(\text{O})\text{NH}$), 137.8, 135.8, 135.7, 134.7, 133.6, 130.8, 129.7, 128.9,

21.2 (*p*-Ph), 21.1 (*p*-Mes), 20.5 (*o*-Mes) ppm. FTIR (KBr pellet): ν_{NH} = 3236 (s) cm^{-1} , ν_{CO} = 1664 (m) cm^{-1} , also 3025 (w), 2966 (w), 2943 (vw), 2912 (w), 2868 (w), 1687 (w), 1612 (w), 1597 (vw), 1569 (vw), 1534 (m), 1486 (vw), 1456 (w), 1386 (w), 1271 (sh), 1263 (w), 1034 (vw), 1017 (vw), 903 (vw), 864 (w), 840 (w), 789 (vw), 746 (vw), 707 (w), 701 (w), 625 (w), 585 (vw), 563 (w), 520 (vw) cm^{-1} . HRMS (ESI pos. ion; NCMe): m/z Calcd, 372.2325; m/z Found, 372.2322 [$\text{M}]^+$.

Data for $\text{H}(\text{O})\text{CNH}(p\text{-MeAr}^{\text{DarF2}})$. Yield: 0.788 g, 1.41 mmol, 72.4%. ^1H NMR analysis $\text{H}(\text{O})\text{CNH}(p\text{-MeAr}^{\text{DarF2}})$ as isolated above indicated a 3:1 mixture of *cis*- and *trans*-isomers. This isomeric mixture was used in the subsequent dehydration step without separation. Spectroscopic data for *cis*-isomer: ^1H NMR (499.8 MHz, CDCl_3 , 20 °C): δ = 7.90 (s, 2H, *p*-ArF), 7.86 (s, 1H, $\text{HC}(\text{O})\text{NH}$), 7.84 (s, 4H, *o*-ArF), 7.28 (s, 2H, *m*-Ph), 6.62 (s, 1H, $\text{HC}(\text{O})\text{NH}$), 2.48 (s, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 20 °C): δ = 160.0 ($\text{HC}(\text{O})\text{NH}$), 141.1, 139.4, 138.5, 131.9 (q, $^2J_{\text{CF}}$ = 33 Hz, *m*-ArF), 131.8, 129.1, 127.1, 123.3 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3), 121.8, (septet, $^3J_{\text{CF}}$ = 4 Hz, *p*-ArF), 21.2 (s, *p*-Me) ppm. ^{19}F NMR (282.3 MHz, C_6D_6): δ = -62.80 (s, CF_3) ppm. Spectroscopic data for *trans*-isomer: ^1H NMR (499.8 MHz, CDCl_3 , 20 °C): δ = 7.91 (s, 2H, *p*-ArF), 7.83 (s, 4H, *o*-ArF), 7.71 (d, 1H, J = 11 Hz, $\text{HC}(\text{O})\text{NH}$), 7.30 (s, 2H, *m*-Ph), 7.01 (d, 1H, J = 11 Hz, $\text{HC}(\text{O})\text{NH}$), 2.49 (s, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 20 °C): δ = 164.1 ($\text{HC}(\text{O})\text{NH}$), 140.3, 138.7, 136.2, 132.5, 132.6 (q, $^2J_{\text{CF}}$ = 33 Hz, *m*-ArF), 129.7, 128.1, 123.1 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3), 122.1 (septet, $^3J_{\text{CF}}$ = 4 Hz, *p*-ArF), 21.1 (s, *p*-Me) ppm. ^{19}F NMR (282.3 MHz, C_6D_6): δ = -62.86 (s, CF_3) ppm. FTIR isomeric mixture (C_6D_6 , KBr windows): ν_{CO} = 1704 (s) cm^{-1} ; ν_{NH} = 3372 (w), 2979 (w), 2923 (w), 2864 (w), 1360 (m), 1280 (vs), 1186 (s), 1133 (vs), 900 (w), 844 (w), 739 (w), 708 (w), 683 (w), 644 (w) cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_{11}\text{F}_2\text{NO}$ (bulk sample, isomeric mixture): C, 50.66; H, 2.03; N, 2.57. Found: C, 50.77; H, 1.84; N, 2.66.

Data for $\text{H}(\text{O})\text{CNH}(p\text{-F}^{\text{DarF2}})$. Yield: 0.913 g, 1.62 mmol, 83.3%. ^1H NMR analysis of $\text{H}(\text{O})\text{CNH}(p\text{-F}^{\text{DarF2}})$ as isolated above indicated a 7:1 mixture of *cis*- and *trans*-isomers. This isomeric mixture was used in the subsequent dehydration step without separation. Spectroscopic data for *cis*-isomer: ^1H NMR (499.8 MHz, CDCl_3 , 20 °C): δ = 7.93 (s, 2H, *p*-ArF), 7.86 (s, 1H, $\text{HC}(\text{O})\text{NH}$), 7.84 (s, 2H, *o*-ArF), 7.21 (d, 2H, $^2J_{\text{FH}}$ = 8 Hz, *m*-Ph), 6.67 (s, 1H, $\text{HC}(\text{O})\text{NH}$), 2.48 (s, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 20 °C): δ = 160.0 ($\text{HC}(\text{O})\text{NH}$), 161.3 (d, $^1J_{\text{CF}}$ = 253 Hz, *p*-Ph), 140.8 (d, $^3J_{\text{CF}}$ = 7 Hz, *o*-Ph), 139.9, 132.2 (q, $^2J_{\text{CF}}$ = 33 Hz, *m*-ArF), 129.0, 125.9, 123.1 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3), 122.4, (septet, $^3J_{\text{CF}}$ = 4 Hz, *p*-ArF), 118.1 (d, $^2J_{\text{CF}}$ = 20 Hz, *m*-Ph) ppm. ^{19}F NMR (282.3 MHz, C_6D_6): δ = -62.85 (s, CF_3), 110.87 (t, $^2J_{\text{FH}}$ = 8 Hz, *p*-Ph) ppm. Spectroscopic data for *trans*-isomer: ^1H NMR (499.8 MHz, CDCl_3 , 20 °C): δ = 7.95 (s, 2H, *p*-ArF), 7.82 (s, 4H, *o*-ArF), 7.70 (d, 1H, J = 11 Hz, $\text{HC}(\text{O})\text{NH}$), 7.25 (d, 2H, J_{FH} = 8 Hz, *m*-Ph), 6.89 (d, 1H, J = 11 Hz, $\text{HC}(\text{O})\text{NH}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 20 °C): δ = 163.7 ($\text{HC}(\text{O})\text{NH}$), 161.1 (d, $^1J_{\text{CF}}$ = 271 Hz, *p*-Ph), 139.1, 138.6 (d, $^3J_{\text{CF}}$ = 9 Hz, *o*-Ph), 132.8 (q, $^2J_{\text{CF}}$ = 33 Hz, *m*-ArF), 129.5, 126.9, 122.9 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3), 122.7 (septet, $^3J_{\text{CF}}$ = 4 Hz, *p*-ArF), 118.8 (d, $^2J_{\text{CF}}$ = 20 Hz, *m*-Ph) ppm. ^{19}F NMR (282.3 MHz, C_6D_6): δ = -62.91 (s, CF_3), 111.18 (t, $^2J_{\text{FH}}$ = 8 Hz, *p*-Ph) ppm. FTIR isomeric mixture (C_6D_6 , KBr windows): ν_{CO} = 1707 (s) cm^{-1} ; ν_{NH} = 3369 (w), 3239 (vw), 3075 (w), 2884 (w), 2279 (s), 1487 (w), 1361 (m), 1276 (vs), 1176 (s), 1137 (vs), 905 (w), 843 (w), 804 (w) cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_{10}\text{F}_3\text{NO}$ (bulk sample, isomeric mixture): C, 49.02; H, 1.78; N, 2.49. Found: C, 49.11; H, 1.84; N, 2.66.

Synthesis of the *m*-Terphenyl Isocyanides ($\text{CNp-R}'\text{Ar}^{\text{R2}})$ (R' = H, Me, F; R = Mes, DarF). Diisopropylamine ($\text{HN}(\text{i-Pr})_2$; 0.520 g, 5.13 mmol, 3.5 equiv) was added, via syringe, to a CH_2Cl_2 solution of $\text{H}(\text{O})\text{CNH}(p\text{-R}'\text{Ar}^{\text{R2}})$ (1.50 mmol, 60 mL). The resulting mixture was stirred vigorously for 5 min and then cooled to 0 °C where POCl_3 (0.450 g, 2.93 mmol, 2 equiv) was added dropwise by syringe over 5 min. The reaction mixture was allowed to warm to room temperature and was then stirred for 3 h. Aqueous Na_2CO_3 (1.5 M, 40 mL) was added and the resulting mixture stirred for 1 h. The organic and aqueous layers were separated and the latter extracted with CH_2Cl_2 (3

× 20 mL). The organic extracts were combined and dried over MgSO_4 . Volatile materials were removed by rotary evaporation. Dissolution of the resulting solid in a minimal amount of NCME followed by cooling to -40°C resulted in the formation of a colorless precipitate, which was collected by filtration and dried *in vacuo*.

Data for $\text{CNp-MeAr}^{\text{Mes2}}$. Yield: 0.345 g, 0.975 mmol, 69.6%. ^1H NMR (499.8 MHz, C_6D_6 , 20°C): δ = 6.87 (s, 4H, *m*-Mes), 6.66 (s, 2H, *m*-Ph), 2.18 (s, 6H, *p*-Mes), 2.08 (s, 12H, *o*-Mes), 1.94 (s, 3H, *p*- CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6 , 20°C): δ = 170.0 (CNR), 139.7, 139.5, 137.7, 135.7, 134.9, 129.9, 128.8, 124.1, 21.2 (*p*-Mes), 21.1 (*p*- CH_3), 20.3 (*o*-Mes) ppm. FTIR (C_6D_6 , KBr windows): ν_{CN} = 2118 cm^{-1} , also 2953 (w), 2924 (w), 2855 (w), 1615 (m), 1488 (sh), 1452 (m), 1377 (w), 1035 (w), 870 (w), 852 (m), 791 (w), 770 (w), 707 (w), 629 (w), 566 (w) cm^{-1} . FTIR (KBr pellet): ν_{CN} = 2121 cm^{-1} , also 3033 (m), 2973 (m), 2912 (w), 2854 (w), 1614 (m), 1599 (m), 1441 (m), 1271 (w), 1248 (vw), 1034 (m), 1012 (m), 866 (s), 852 (m), 794 (m), 769 (m), 748 (w), 707 (m), 628 (m), 588 (w), 564 (m), 522 (w) cm^{-1} . Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{N}$: C, 88.34; H, 7.70; N, 3.96. Found: C, 88.24; H, 7.49; N, 3.90.

Data for $\text{CNp-MeAr}^{\text{DArF}}$. Yield: 0.336 g, 1.11 mmol, 74.4%. ^1H NMR (499.8 MHz, C_6D_6 , 20°C): 7.76 (s, 2H, *p*-ArF), 7.70 (s, 4H, *o*-ArF), 6.44 (s, 2H, *m*-Ph), 1.87 (s, 3H, *p*-Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6 , 20°C): δ = 174.8 (CNR), 140.29, 139.3, 136.7, 132.2 (q, $^2J_{\text{CF}}$ = 33 Hz, *m*-ArF), 131.0, 129.6, 127.6, 123.7 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3), 122.5 (septet, $^3J_{\text{CF}}$ = 4 Hz, *p*-ArF), 20.9 (s, *p*-Me) ppm. ^{19}F NMR (282.3 MHz, C_6D_6 , 20°C): δ = -63.19 (s, CF_3) ppm. FTIR (C_6D_6 , KBr window): ν_{CN} = 2118 (s) cm^{-1} , also 3098 (w), 2962 (w), 2926 (w), 1621 (w), 1596 (w), 1463 (w), 1399 (m), 1369 (s), 1310 (w), 1277 (vs), 1247 (w), 1191 (m), 1174 (m), 1161 (m), 1127 (s), 905 (m), 869 (w), 849 (w), 705 (m), 683 (m), 647 (w) cm^{-1} . FTIR (KBr pellet): ν_{CN} = 2118 (s) cm^{-1} , also 3099 (vw), 2927 (vw), 2848 (vw), 1622 (w), 1597 (w), 1465 (w), 1405 (m), 1370 (m), 1314 (m), 1278 (vs), 1246 (w), 1189 (s), 1178 (s), 1165 (s), 1125 (vs), 1114 (s), 1073 (m), 951 (w), 906 (s), 869 (m), 848 (m), 708 (s), 681 (s) cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_9\text{F}_{12}\text{N}$: C, 52.39; H, 1.72; N, 2.66. Found: C, 52.07; H, 1.65; N, 2.70.

Data for $\text{CNp-FAr}^{\text{DArF}}$. Yield: 0.428 g, 0.790 mmol, 52.4%. ^1H NMR (499.8 MHz, C_6D_6 , 20°C): δ = 7.75 (s, 2H, *p*-ArF), 7.57 (s, 4H, *o*-ArF), 6.28 (d, 2H, $^2J_{\text{FH}}$ = 8 Hz, *m*-Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6 , 20°C): δ = 175.1 (CNR), 161.7 (d, $^1J_{\text{CF}}$ = 254 Hz, *p*-Ph), 139.0 (d, $^3J_{\text{CF}}$ = 9 Hz, *o*-Ph), 137.9, 132.4 (q, $^2J_{\text{CF}}$ = 33 Hz, *m*-ArF), 129.5, 127.5, 123.5 (q, $^1J_{\text{CF}}$ = 273 Hz, CF_3), 123.0 (septet, $^3J_{\text{CF}}$ = 4 Hz, *p*-ArF), 119.4, 117.5 (d, $^2J_{\text{CF}}$ = 20 Hz, *m*-Ph) ppm. ^{19}F NMR (282.3 MHz, C_6D_6): δ = -62.9 (s, CF_3), -107.3 (t, $^2J_{\text{FH}}$ = 8 Hz, *p*-Ph) ppm. FTIR (C_6D_6 , KBr window): ν_{CN} = 2113 (s) cm^{-1} , also 2964 (w), 2920 (w), 2848 (w), 1596 (vw), 1398 (vw), 1364 (m), 1280 (vs), 1186.4 (s), 1143 (s), cm^{-1} . FTIR (KBr pellet): ν_{CN} = 2118 (s) cm^{-1} , also 3090 (w), 2926 (w), 2851 (w), 1624 (w), 1596 (m), 1463 (m), 1424.2 (m), 1366 (s), 1285 (s), 1224 (m), 1154 (vs), 1133 (vs), 1069 (s), 908 (s), 874 (m), 847 (m), 736 (m), 633 (m), 683 (s) cm^{-1} . HRMS (ESI neg. ion; NCME): m/z Calcd, 544.0376; m/z Found, 544.0384 [$\text{M}]^-$.

Synthesis of $\text{CN}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)$. Diisopropylamine ($\text{HN}(i\text{-Pr})_2$; 1.06 g, 10.50 mmol, 2.7 equiv) was added, via syringe, to a stirring CH_2Cl_2 solution of $\text{HC(O)NH}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)$ (1.00 g, 3.89 mmol, 60 mL) under a N_2 atmosphere. The resulting mixture was cooled to 0°C and allowed to equilibrate for 5 min. POCl_3 (0.656 g, 4.28 mmol, 1.1 equiv) was then added dropwise via syringe over 10 min. The reaction mixture was then allowed to warm to room temperature and react for 24 h. Aqueous Na_2CO_3 (1.5 M, 40 mL) was added and the resulting mixture stirred for 1 h. The organic and aqueous layers were separated and the latter extracted with CH_2Cl_2 (3 × 20 mL). The organic extracts were combined and dried over MgSO_4 . Volatile materials were removed by rotary evaporation to afford a crude oil, which was purified by column chromatography (silica gel) with CH_2Cl_2 as an eluent to afford $\text{CN}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)$ as a low-melting solid. Yield: 0.499, 2.09 mmol, 53.7%. ^1H NMR (499.8 MHz, C_6D_6): δ = 7.32 (s, 1H), 6.76 (s, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, C_6D_6): δ = 171.6 (CNR), 132.7 (q, $^2J_{\text{CF}}$ = 34 Hz, *m*-ArF), 126.6 (m, *i*-ArF and *o*-ArF), 122.5 (q, $^1J_{\text{CF}}$ = 274 Hz, CF_3), 122.4 (septet, $^3J_{\text{CF}}$ = 4 Hz, *p*-

ArF) ppm. ^{19}F NMR (470.6 MHz, C_6D_6): δ = -62.7 (s, CF_3) ppm. FTIR (C_6D_6 , KBr window): ν_{CN} = 2129 (vs) cm^{-1} , also 3088 (vw), 3062 (vw), 2928 (vw), 1622 (w), 1459 (m), 1369 (vs), 1281 (vs), 1249 (s), 1179 (vs), 1145 (vs), 1107 (m), 1047 (vw), 898 (s), 847 (m), 741 (vw), 723 (w), 685 (m) cm^{-1} . MS (electron impact, NCME): m/z Calcd, 239.0; m/z Found, 239.0 [$\text{M}]^-$.

Synthesis of $\text{Cr}(\text{CNR})(\text{CO})_5$ Complexes (1–18). A 350 mL resealable ampoule was charged with a THF solution of $\text{Cr}(\text{CO})_6$ (1.00 g, 4.54 mmol, 100 mL, 10 equiv). The solution was then subjected to three freeze–pump–thaw cycles. The ampoule was then sealed and warmed to room temperature where it was irradiated for 2 h using a mercury arc lamp (Oriel Corporation, model 66023, 1000 W). During this time, the reaction mixture turned from colorless to bright yellow with visible effervescence of CO, indicating the formation of $\text{Cr}(\text{THF})(\text{CO})_5$. The resulting mixture was then combined with a THF solution (4.54 mM) of isocyanide (1.0 equiv) and allowed to stir for 2 h. All volatile materials were then removed under reduced pressure. Unreacted $\text{Cr}(\text{CO})_6$ was then recovered from the solid product mixture by sublimation (50 mTorr, 40°C). The resulting residue was then extracted with C_6H_6 and filtered through Celite. The pale yellow to colorless filtrate was then evaporated to dryness under reduced pressure. The resulting solid was dissolved in a minimal amount of *n*-pentane and then stored at -35°C . The single crystals thereby produced were collected and dried *in vacuo*. Full characterization details for all complexes are provided in the Supporting Information.

Crystallographic Structure Determinations. Single-crystal X-ray structure determinations were carried out using Bruker Platform or Kappa X-ray Diffractometers equipped with Mo or Cu radiation sources (sealed tube or rotating anode), low-temperature cryostats, and CCD detectors (Bruker APEX or Bruker APEX II). All structures were solved by direct methods using SHEX⁷³ and refined by full-matrix least-squares procedures utilizing SHELXL⁷³ within the Olex2 small-molecule solution, refinement and analysis software package.⁷⁴ Crystallographic data-collection and refinement information are listed in Table S3.1 (Supporting Information). Full details of disorder modeling and structure refinement are provided in the Supporting Information.

■ ASSOCIATED CONTENT

● Supporting Information

Characterization data for $\text{Cr}(\text{CNR})(\text{CO})_5$ complexes 1–18, Cotton–Kraihanzel force constant (*k*) calculations and $\delta_{13\text{C}}$ vs k_n plots, crystallographic structure determinations, and cif. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jsfig@ucsd.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the U.S. Department of Energy (DE-SC0008058) for support of this work. The U.S. National Science Foundation is acknowledged for Graduate Research Fellowships to A.E.C. and C.C.M. The California Institute for Telecommunications and Information Technology (CalIT²) is thanked for an undergraduate summer research scholarship to D.S.R. J.S.F. is a Camille Dreyfus Teacher Scholar (2012–2017). We also thank Professors William C. Troglor and Mikhail V. Barybin for very helpful discussions.

REFERENCES

- (1) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Transition Metals*; Wiley: New York, 1969.
- (2) Cotton, F. A.; Zingales, F. J. *Am. Chem. Soc.* **1961**, *83*, 351.
- (3) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 3021.
- (4) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.
- (5) Bonati, F.; Minghetti, G. *Inorg. Chim. Acta* **1974**, *9*, 95.
- (6) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247.
- (7) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193.
- (8) King, R. B.; Saran, M. S. *Inorg. Chem.* **1974**, *13*, 74.
- (9) Weber, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1515.
- (10) Carofiglio, T.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1989**, *28*, 4417.
- (11) Barybin, M. V.; Young, V. G.; Ellis, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 4678.
- (12) Connor, J. A.; Jones, E. M.; McEwen, G. K.; Lloyd, M. K.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1246.
- (13) Essenmacher, G. J.; Treichel, P. M. *Inorg. Chem.* **1977**, *16*, 800.
- (14) Treichel, P. M.; Mueh, H. J. *Inorg. Chem.* **1977**, *16*, 1167.
- (15) Johnston, R. F.; Cooper, J. C. *J. Mol. Struct.: THEOCHEM* **1991**, *236*, 297.
- (16) Lentz, D. *Chem. Ber.* **1984**, *117*, 415.
- (17) Lentz, D. *J. Organomet. Chem.* **1990**, *381*, 205.
- (18) Lentz, D. *Angew. Chem., Int. Ed.* **1994**, *33*, 1315.
- (19) Lentz, D.; Anibarro, M.; Preugschat, D.; Bertrand, G. *J. Fluorine Chem.* **1998**, *89*, 73.
- (20) Barybin, M. V.; Brennessel, W. W.; Kucera, B. E.; Minyaev, M. E.; Sussman, V. J.; Young, V. G.; Ellis, J. E. *J. Am. Chem. Soc.* **2007**, *129*, 1141.
- (21) Barybin, M. V. *Coord. Chem. Rev.* **2010**, *254*, 1240.
- (22) Fox, B. J.; Sun, Q. Y.; DiPasquale, A. G.; Fox, A. R.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2008**, *47*, 9010.
- (23) Ditri, T. B.; Fox, B. J.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2009**, *48*, 8362.
- (24) Fox, B. J.; Millard, M. D.; DiPasquale, A. G.; Rheingold, A. L.; Figueroa, J. S. *Angew. Chem., Int. Ed.* **2009**, *48*, 3473.
- (25) Labios, L. A.; Millard, M. D.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 11318.
- (26) Margulieux, G. W.; Weidemann, N.; Lacy, D. C.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 5033.
- (27) Ditri, T. B.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2011**, *50*, 10448.
- (28) Emerich, B. M.; Moore, C. E.; Fox, B. J.; Rheingold, A. L.; Figueroa, J. S. *Organometallics* **2011**, *30*, 2598.
- (29) Stewart, M. A.; Moore, C. E.; Ditri, T. B.; Labios, L. A.; Rheingold, A. L.; Figueroa, J. S. *Chem. Commun.* **2011**, 47, 406.
- (30) Tomson, N. C.; Labios, L. A.; Weyhermuller, T.; Figueroa, J. S.; Wieghardt, K. *Inorg. Chem.* **2011**, *50*, 5763.
- (31) Carpenter, A. E.; Margulieux, G. W.; Millard, M. D.; Moore, C. E.; Weidemann, N.; Rheingold, A. L.; Figueroa, J. S. *Angew. Chem., Int. Ed.* **2012**, *51*, 9412.
- (32) Carpenter, A. E.; Wen, I.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Chem.—Eur. J.* **2013**, *19*, 10452.
- (33) Ditri, T. B.; Carpenter, A. E.; Ripatti, D. S.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2013**, *52*, 13216.
- (34) Barnett, B. R.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2014**, *136*, 10262.
- (35) Carpenter, A. E.; McNeece, A. J.; Barnett, B. R.; Estrada, A. L.; Mokhtarzadeh, C. C.; Moore, C. E.; Rheingold, A. L.; Perrin, C. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2014**, *136*, 15481.
- (36) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.
- (37) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773.
- (38) Clyburne, J. A. C.; McMullen, N. *Coord. Chem. Rev.* **2000**, *210*, 73.
- (39) Robinson, G. H. *Chem. Commun.* **2000**, 2175.
- (40) Power, P. P. *Chem. Commun.* **2003**, 2091.
- (41) Power, P. P. *Organometallics* **2007**, *26*, 4362.
- (42) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047.
- (43) Kays, D. L. *Dalton Trans.* **2011**, *40*, 769.
- (44) Power, P. P. *Chem. Rev.* **2012**, *112*, 3482.
- (45) Burdett, J. K. *Inorg. Chem.* **1975**, *14*, 375.
- (46) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.
- (47) Poliakoff, M.; Turner, J. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2809.
- (48) Zhou, M.; Andrews, L.; Bauschlicher, C. W. *Chem. Rev.* **2001**, *101*, 1931.
- (49) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.
- (50) Gansow, O. A.; Kimura, B. Y.; Dobson, G. R.; Brown, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 5922.
- (51) Cronin, D. L.; Wilkinson, J. R.; Todd, L. J. *J. Magn. Reson.* **1975**, *17*, 353.
- (52) Gavenonis, J.; Tilley, T. D. *Organometallics* **2004**, *23*, 31.
- (53) For other examples of *m*-terphenyl isocyanide synthesis using Pd-catalyzed cross-coupling, see: (a) Tanabiki, M.; Tsuchiya, K.; Kumanomido, Y.; Matsubara, K.; Motoyama, Y.; Nagashima, H. *Organometallics* **2004**, *23*, 3976. (b) Ito, H.; Kato, T.; Sawamura, M. *Chem. Lett.* **2006**, *35*, 1038. (c) Ito, H.; Kato, T.; Sawamura, M. *Chem.—Asian J.* **2007**, *2*, 1436.
- (54) Sattler, W.; Parkin, G. *Chem. Commun.* **2009**, 7566.
- (55) Drummond Murdoch, H.; Henzi, R. *J. Organomet. Chem.* **1966**, *5*, 166.
- (56) Fehllhammer, W. P.; Bartel, K.; Voelkl, A.; Achatz, D. *Z. Anorg. Chem.* **1982**, *37B*, 1044.
- (57) Albers, M. O.; Coville, N. J.; Ashworth, T. V.; Singleton, E.; Swanepoel, H. E. *J. Organomet. Chem.* **1980**, *199*, 55.
- (58) Yu, M. P. Y.; Yam, V. W.-W.; Cheung, K.-K.; Mayr, A. *J. Organomet. Chem.* **2006**, *691*, 4514.
- (59) Smith, R. C.; Shah, S.; Urnezis, E.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2002**, *125*, 40.
- (60) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.
- (61) Brennessel, W. W.; Ellis, J. E. *Angew. Chem., Int. Ed.* **2007**, *46*, 598.
- (62) While the Cotton–Kraihanzel force constant calculation method is known to be an oversimplification, acceptable quantitative results are obtained when comparing a homologous series of complexes or complexes possessing identical symmetry elements. See: (a) Jones, L. H. *Inorg. Chem.* **1968**, *7*, 1681. (b) Cotton, F. A. *Inorg. Chem.* **1968**, *7*, 1683.
- (63) The Cambridge Structural Database (CSD v 5.35, Nov. 2013) contains 615 unique transition-metal complexes of CNXyl. For representative homoleptic complexes of CNXyl, see: (a) Yamamoto, Y.; Yamazaki, H. *J. Organomet. Chem.* **1985**, *282*, 191. (b) Warnock, G. F.; Cooper, N. J. *Organometallics* **1989**, *8*, 1826. (c) Leach, P. A.; Geib, S. J.; Corella, J. A.; Warnock, G. F.; Copper, N. J. *J. Am. Chem. Soc.* **1994**, *116*, 8566. (d) Barybin, M. V.; Young, V. G.; Ellis, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 4678.
- (64) It is important to note that, when using the C–K force constant approximation, only k_2 for the equatorial carbonyl ligands of a C_{4v} -symmetric complex can be directly compared to a homoleptic complex with O_h symmetry (e.g., $Cr(CO)_6$). See ref 49.
- (65) Lentz, D.; Graske, K.; Preugschat, D. *Chem. Ber.* **1988**, *121*, 1445.
- (66) Lentz, D.; Preugschat, D. *Acta Crystallogr., Sect. C* **1993**, *49*, 52.
- (67) Olaru, M.; Beckmann, J.; Rač, C. I. *Organometallics* **2014**, *33*, 3012.
- (68) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- (69) Arnarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Elsevier: Oxford, 2003.
- (70) A. Mironov, M.; S. Mokrushin, V. *Mendeleev Commun.* **1998**, *8*, 242.
- (71) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.
- (72) Huffman, C. W. *J. Org. Chem.* **1958**, *23*, 727.
- (73) Sheldrick, G. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
- (74) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.