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Isolable, Copper(I) Dicarbonyl Complexes Supported by *N*-Heterocyclic Carbenes

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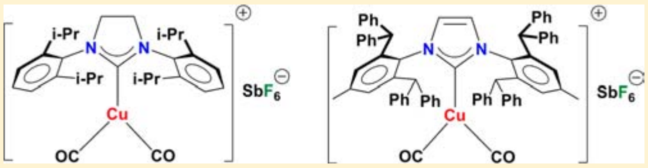
Supporting Information

ABSTRACT: Cationic copper(I) dicarbonyl complexes supported by *N*-heterocyclic carbene ligands, SIPr and IPr*, have been synthesized. [(SIPr)Cu(CO)$_2$][SbF$_6$] and [(IPr*)Cu(CO)$_2$][SbF$_6$] have a trigonal planar, three-coordinate copper atom with an average Cu−CO distance of 1.915 Å and display C−O stretching frequencies higher than that of the free CO (2143 cm^{-1}). The high CO stretching frequencies suggest that the Cu(I)−CO interaction in these cationic adducts is dominated by electrostatic and OC → Cu σ-donor components. [(SIPr)Cu(CO)$_2$][SbF$_6$] and [(IPr*)Cu(CO)$_2$][SbF$_6$] readily form the corresponding [(SIPr)Cu(CO)(H$_2$O)][SbF$_6$] and [(IPr*)Cu(CO)(H$_2$O)][SbF$_6$] with loss of a CO even with traces of water, but they can be converted back to the dicarbonyl adducts using excess CO. The synthesis and structure of [(IPr*)Cu(H$_2$O)][SbF$_6$] are also reported. It is a two-coordinate copper adduct with a Cu−O distance of 1.874(2) Å. It reacts with excess CO to form [(IPr*)Cu(CO)$_2$][SbF$_6$].



INTRODUCTION

Copper plays an important role in many processes involving carbon monoxide.[1−9] For example, Cu(I)/ZnO catalyzes the synthesis of methanol from syngas and mediates a low-temperature water−gas shift reaction.[10,11] Copper salts have also been used in selective removal of CO from industrial gas streams.[12−14] In addition, CO is often used as a probe ligand during the study of reduced copper-containing proteins and enzymes.[5,15] Overall, copper carbonyl adducts are of significant interest due to a number of reasons. Although the chemistry between copper salts and CO was described over 100 years ago,[1,2] copper carbonyl adducts such as Cu(CF$_3$CO$_2$)CO that can be isolated as analytically pure solids and are stable in the absence of CO came to prominence only after the late 1960s.[16] There are a fair number and variety of thermally stable and well-authenticated copper(I) monocarbonyl adducts presently known.[2,17−24]

Molecules bearing more than one carbon monoxide on a copper site are rare. Souma and co-workers demonstrated that copper binds to more than one CO ligand in strongly acidic media (e.g., neat FSO$_3$H).[25] Such copper(I) polycarbonyl adducts are also of interest as they catalyze the carbonylation of olefins, alcohols, and even saturated hydrocarbons.[26,27] Several other copper(I) polycarbonyls have also been generated using weakly coordinating counteranions such as AsF$_6^-$ and N(SO$_2$CF$_3$)$_2^-$,[3,28,29] weakly basic sites in zeolite host lattices as counteranions,[30−32] and in the gas phase.[33,34] Structurally characterized copper(I) polycarbonyls are exceedingly rare, and they include Cu(CO)$_2$N(SO$_2$CF$_3$)$_2$, Cu(CO)$_2$(1-Bn-CB$_{11}$F$_{11}$), and [Cu(CO)$_4$][1-Et-CB$_{11}$F$_{11}$] (Figure 1) reported by Strauss and co-workers.[28,35]

In this paper, we report the isolation of two new cationic copper(I)−dicarbonyl complexes [(SIPr)Cu(CO)$_2$][SbF$_6$] and [(IPr*)Cu(CO)$_2$][SbF$_6$] (Figure 2) supported by *N*-heterocyclic carbene ligands (SIPr = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene and IPr* = 1,3-bis(2,6-bis-(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene). These complexes are the first dicarbonyl complexes of copper stabilized by strongly σ-donating *N*-heterocyclic carbene ligands.[36,37] We are also reporting the synthesis and structure of a copper(I)−water adduct.

RESULTS AND DISCUSSION

The copper(I) dicarbonyl complex [(SIPr)Cu(CO)$_2$][SbF$_6$] (**4**) was synthesized by treating a dichloromethane solution of (SIPr)CuBr with AgSbF$_6$ in the presence of carbon monoxide (1 atm). [(SIPr)Cu(CO)$_2$][SbF$_6$] is a colorless solid and was characterized by NMR and IR spectroscopy, elemental analysis, and X-ray crystallography. The room-temperature ^{13}C{^{1}H} NMR spectrum of [(SIPr)Cu(CO)$_2$][SbF$_6$] in CD$_2$Cl$_2$ showed the carbene carbon resonance at δ 200.3, which is upfield of the carbene carbon resonance for [(SIPr)CuCF$_3$] (204.5 ppm)[38] and downfield compared to [(SIPr)Au(CO)][SbF$_6$] (195.4 ppm).[39] The carbene carbon chemical shift of [(SIPr)Cu(CO)$_2$][SbF$_6$] (200.3 ppm) is comparable to other reported cationic copper carbene complexes like [(SIPr)$_2$Cu][PF$_6$] (199.8 ppm).[40] For comparison, the ^{13}C signal of the carbene carbon of metal-free SIPr appears at 243.8 ppm (in benzene-d_6). We could not observe the carbon resonance corresponding to CO in the ^{13}C NMR spectrum, which is not unusual for copper−carbonyls.[41]

X-ray-quality crystals of [(SIPr)Cu(CO)$_2$][SbF$_6$] were obtained from a dichloromethane−hexane solution at −10

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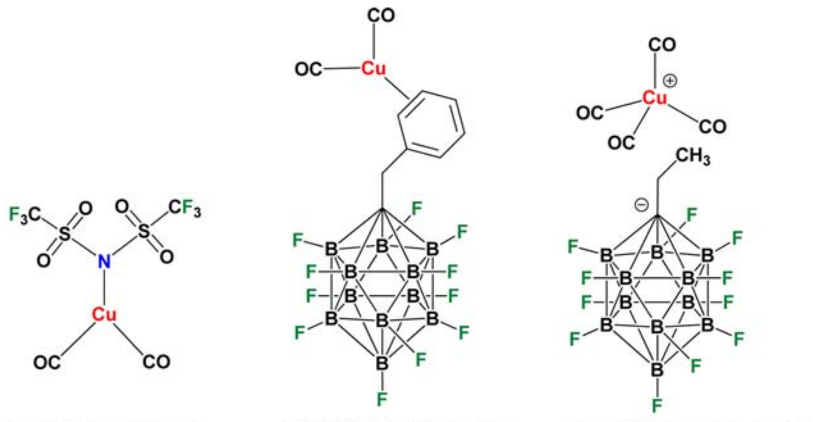
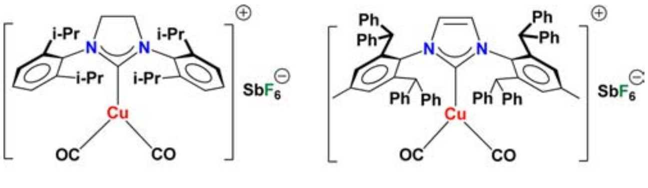


Cu(CO)$_2$N(SO$_2$CF$_3$)$_2$ (1) Cu(CO)$_2$(1-Bn-CB$_{11}$F$_{11}$) (2) [Cu(CO)$_4$][1-Et-CB$_{11}$F$_{11}$] (3)

Figure 1. Structurally characterized copper(I) polycarbonyl complexes.



[(SIPr)Cu(CO)$_2$][SbF$_6$] (4) [(IPr*)Cu(CO)$_2$][SbF$_6$] (5)

Figure 2. *N*-Heterocyclic carbene ligand-supported copper(I) dicarbonyl complexes.

°C. The X-ray structure (Figure 3) revealed that the copper center in [(SIPr)Cu(CO)$_2$][SbF$_6$] displays a trigonal planar geometry (sum of the angles at copper = 358.5°) with an OC−Cu−CO angle of 119.77(10)°. The SbF$_6^-$ counteranion lies closer to the copper center with one Cu···F contact at 2.494 Å (which is within the sum of the van der Waals radii of Cu and F = 2.87 Å). However, as evident from the angles involving the CCu(CO)$_2$ moiety noted above, this interaction is not strong enough to distort the copper from the trigonal planar geometry. The Cu−C(carbene) bond length of 1.964(2) Å is comparable to that reported for the cationic *N*-heterocyclic carbene copper(I) complexes like [(SIPr)$_2$Cu][PF$_6$] (2.000(15) Å).[40]

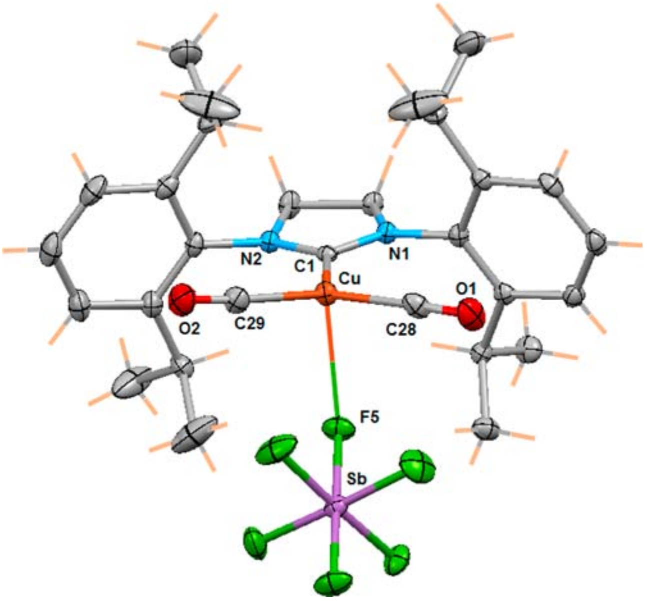


Figure 3. Molecular structure showing [(SIPr)Cu(CO)$_2$][SbF$_6$] (**4**); ellipsoids are shown at the 40% probability level. Selected bond distances (Angstroms) and angles (degrees): Cu−C1 1.964(2), Cu−C28 1.925(2), Cu−C29 1.906(2), C28−O1 1.120(3), C29−O2 1.110(3), C1−N1 1.335(3), C1−N2 1.341(3), Sb−F5 1.8958(13), F5···Cu 2.494; C28−Cu−C1 119.28(9), C29−Cu−C1 119.47(9), C28−Cu−C29 119.77(10), O1−C28−Cu 174.7(2), O2−C29−Cu 174.6(2), Cu−C1−N1 124.78(14), Cu−C1−N2 127.31(14).

The Cu−CO bond distances of [(SIPr)Cu(CO)$_2$][SbF$_6$] are 1.925(2) and 1.906(2) Å. There are only two structurally characterized copper(I) dicarbonyl adducts in the open literature, and a comparison of metric parameters shows that they also have similar Cu−CO distances, e.g., Cu(CO)$_2$(N(SO$_2$CF$_3$)$_2$) [1.895(6), 1.906(6) Å] and Cu(CO)$_2$(1-Bn-CB$_{11}$F$_{11}$) [1.915(3), 1.916(3) Å]. [N{(C$_3$F$_7$)C(2-F,6-(CF$_3$)-C$_6$H$_3$)N}$_2$]CuCO is an example of a copper monocarbonyl adduct with a three-coordinate copper center. It has a much shorter Cu−CO bond at 1.813(5) Å.[42]

The IR spectrum of [(SIPr)Cu(CO)$_2$][SbF$_6$] in KBr pellets shows two bands attributable to CO stretch at 2149(s) and 2168(m) cm^{-1}. These values are higher than that of the free CO ($\overline{\upsilon}_{CO}$ = 2143 cm^{-1}) but comparable to those of Cu(CO)$_2$(CF$_3$SO$_3$)[43] ($\overline{\upsilon}_{CO}$ = 2143(s), 2171(m) cm^{-1}) and Cu(CO)$_2$(zeolite-Y)[30,44] (2150(s), 2178(m) cm^{-1}) (Table 1). High $\overline{\upsilon}_{CO}$ values of [(SIPr)Cu(CO)$_2$][SbF$_6$] are probably a result of an electrostatic effect and primarily σ-type Cu−CO interaction with low Cu → CO π-back-donation.[3,7] In addition to the two bands noted above, KBr pellets prepared using [(SIPr)Cu(CO)$_2$][SbF$_6$] also showed two other bands at 2144 and 2133 cm^{-1} in the typical terminal CO stretch region. Unlike the 2149 and 2168 cm^{-1} set which decreases in intensity simultaneously at the same proportion upon standing or evacuation, the two bands at 2133 and 2144 cm^{-1} vary their intensity independent of each other at different rates. This suggests that they are possibly due to two different species resulting from decomposition of [(SIPr)Cu(CO)$_2$][SbF$_6$]. When the solid samples of [(SIPr)Cu(CO)$_2$][SbF$_6$] were exposed to air/moisture, the intensity of $\overline{\upsilon}_{CO}$ peak at 2133 cm^{-1} increased in the IR spectrum, suggesting that one of these species may be a water adduct like [(SIPr)Cu(CO)(H$_2$O)]-[SbF$_6$]. Note that Cu^I(CO)(H$_2$O)(zeolite-ZSM-5) has been reported and has a ν_{CO} band at 2130 cm^{-1}.[45] Indeed, it is possible to synthesize [(SIPr)Cu(CO)(H$_2$O)][SbF$_6$] by purging CO from a dichloromethane solution of [(SIPr)Cu-(CO)$_2$][SbF$_6$] using N$_2$ gas that has some moisture. [(SIPr)-

Table 1. Comparison of Vibrational ($\bar{\upsilon}_{CO}$, cm^{-1}) and Structural (bond distances, Angstroms) Properties for Several Copper(I) Dicarbonyl Compounds, $Cu(CO)_2^+$

compound	$\bar{\upsilon}_{CO}$ cm^{-1}	Cu−CO, Å	C−O, Å	refs
CO	2143		1.12822(7)	55−57
$Cu(CO)_2$(zeolite-Y)	2150(s), 2178(m)			30,44
$Cu(CO)_2(AsF_6)$	2164, 2177[a]			29
$Cu(CO)_2$(zeolite-ZSM-5)	2151(s), 2178(m)			32,45
$Cu(CO)_2(NH_3)$(zeolite-ZSM-5)	2128, 2158			45
$Cu(CO)_2$(zeolite-MFI)	2151(s), 2177(m)			31
$Cu(CO)_2(CF_3SO_3)$	2143(s), 2171(m)			43
$Cu(CO)_2$(1-Et-$CB_{11}F_{11}$)	2168(s), 2189(m)			35
$Cu(CO)_2$(1-Bn-$CB_{11}F_{11}$)	2166(s), 2184(m)	1.915(3)	1.109(3)	35
		1.916(3)	1.115(3)	
$Cu(CO)_2(N(SO_2CF_3)_2)$	2158(s), 2184(m)	1.895(6)	1.115(7)	28
		1.906(6)	1.130(7)	
$[(SIPr)Cu(CO)_2][SbF_6]$	2149(s), 2168(m)	1.906(2)	1.110(3)	this work
		1.925(2)	1.120(3)	
$[(IPr^*)Cu(CO)_2][SbF_6]$	2151(s), 2171(m)	1.883(7)	1.108(8)	this work
		1.948(7)	1.132(8)	

[a] From Raman spectrum.

$Cu(CO)(H_2O)][SbF_6]$ was characterized by NMR, IR spectroscopy, and elemental analysis. It displays a strong band at 2133 cm^{-1} in the IR spectrum that can be assigned to the CO stretch. It is possible to obtain $[(SIPr)Cu(CO)_2][SbF_6]$ back by treating a dichloromethane solution of $[(SIPr)Cu(CO)(H_2O)][SbF_6]$ with excess CO. The species that produced the 2144 cm^{-1} band in the IR spectrum may be $[(SIPr)Cu(CO)][SbF_6]$, but we have no conclusive evidence at this point. Attempted synthesis of $[(SIPr)Cu(CO)][SbF_6]$ using limited amounts of CO always produced a mixture of compounds which also includes $[(SIPr)Cu(CO)_2][SbF_6]$. Solid $[(SIPr)Cu(CO)_2][SbF_6]$ loses CO almost completely if exposed to reduced pressure for prolonged periods (∼8 h) as evident from the disappearance of the CO band in the IR spectrum.

We thought that it may be possible to synthesize a related copper(I) monocarbonyl using a sterically more demanding NHC supporting ligand.[46−48] Accordingly, we prepared (IPr*)CuBr (using IPr*HCl salt, KO^{t}Bu, and $Me_2S{\cdot}CuBr$) that has a much bulkier carbene and treated it with $AgSbF_6$ in the presence of carbon monoxide (1 atm). The IR spectrum of the resulting product $[(IPr^*)Cu(CO)_2][SbF_6]$ (**5**) displayed two bands at 2151(s) and 2171(m) cm^{-1} in the CO stretch region, similar to that observed for $[(SIPr)Cu(CO)_2][SbF_6]$, suggesting that it is still a copper(I) dicarbonyl complex (instead of a monocarbonyl). We also observed two additional peaks at 2135 and 2143 cm^{-1} in the IR spectrum, suggesting some decomposition of $[(IPr^*)Cu(CO)_2][SbF_6]$ (**5**), leading to formation of other CO-containing products during sample preparation and IR data collection. Compound $[(IPr^*)Cu(CO)_2][SbF_6]$ is relatively less stable than the $[(SIPr)Cu(CO)_2][SbF_6]$ complex. Note also that $[(IPr^*)Cu(CO)_2][SbF_6]$ has an imidazol-2-ylidene system rather than imidazolin-2-ylidene supporting ligand. Upon exposure to even traces of moisture or air, $[(IPr^*)Cu(CO)_2][SbF_6]$ forms $[(IPr^*)Cu(CO)(H_2O)][SbF_6]$, which can be further converted to $[(IPr^*)Cu(H_2O)][SbF_6]$ by placing it under reduced pressure for several hours. We also synthesized and characterized the copper(I) aqua complex $[(IPr^*)Cu(H_2O)][SbF_6]$ independently from reaction of (IPr*)CuBr and $AgSbF_6$ in dichloromethane solution. The X-ray structure of $[(IPr^*)Cu(H_2O)][SbF_6]$ is illustrated in Figure 4. It has a two-coordinate copper center with a relatively short Cu−O bond (1.874(2) Å). Such well-authenticated Cu(I)−water adducts are not very common.[49−51] The Cu(I)−OH_2 bond length observed in $[(IPr^*)Cu(H_2O)][SbF_6]$ can be compared to the corresponding distance of copper(I)−water adducts like $\{[Cu(2,3\text{-diphenylquinoxaline})(H_2O)]ClO_4\}_n$ [2.154(6) Å][49] and $[Cu\{CR^1(OR^2)\}(MeCN)(H_2O)][PF_6]$ (R^1 = (*E*)-CH=CH-2-furyl, R^2 = (1*R*,2*S*,5*R*)-menthyl), (2.361(9) Å)].[50] The latter two adducts have longer Cu−O distances, but they are however three-coordinate copper adducts in contrast to the two-coordinate $[(IPr^*)Cu(H_2O)][SbF_6]$. Bubbling excess CO through a dichloromethane solution of $[(IPr^*)Cu(H_2O)][SbF_6]$ leads to $[(IPr^*)Cu(CO)_2][SbF_6]$. Thus, [(IPr*)Cu-

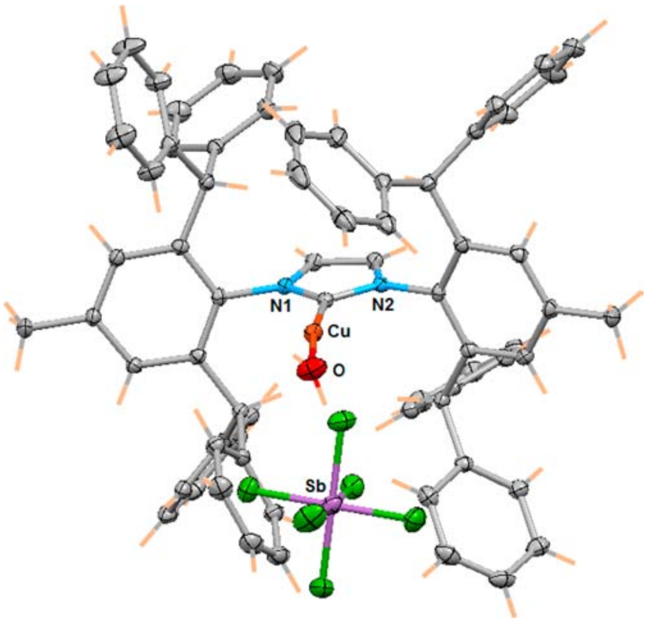


Figure 4. Molecular structure showing $[(IPr^*)Cu(H_2O)][SbF_6]$; ellipsoids are shown at the 40% probability level. Selected bond distances (Angstroms) and angles (degrees): Cu−C1 1.870(2), Cu−O 1.874(2), N1−C1 1.356(3), N2−C1 1.360(3); C1−Cu−O 172.67(10), Cu−C1−N1 131.16(16), Cu−C1−N2 125.30(16), N1−C1−N2 103.54(18).

$(CO)_2][SbF_6]$ and $[(IPr^*)Cu(H_2O)][SbF_6]$ can be reversibly converted to each other using appropriate conditions.

The X-ray structure of $[(IPr^*)Cu(CO)_2][SbF_6]$ (Figure 5) revealed that it is indeed a dicarbonyl adduct. It produced weakly diffracting crystals and crystallizes with one molecule of dichloromethane in the asymmetric unit. In contrast to $[(SIPr)Cu(CO)_2][SbF_6]$, the copper center in $[(IPr^*)Cu(CO)_2][SbF_6]$ shows a somewhat distorted trigonal planar coordination with C−Cu−C angles of 129.7(3)°, 118.6(3)°, and 110.5(3)°. The $Cu-C_{carbene}$ distance of $[(IPr^*)Cu(CO)_2][SbF_6]$ (1.947(5) Å) is longer than the corresponding distance found for the two-coordinate copper(I) aqua complex $[(IPr^*)Cu(H_2O)][SbF_6]$ (1.870(2) Å), which is not surprising. $[(IPr^*)Cu(CO)_2][SbF_6]$ displays two different Cu−CO bond distances at 1.948(7) and 1.883(7) Å, but the average Cu−CO distance of 1.915 Å is the same as that observed for $[(SIPr)Cu(CO)_2][SbF_6]$ (av. Cu−CO 1.915 Å). The $Cu(CO)_2$ and carbene−NCN fragments of $[(IPr^*)Cu(CO)_2][SbF_6]$ adopt a more staggered conformation as evident from the $N_2C_{carbene}Cu$ and $C_{carbene}CuC_2$ plane twist angle of 43.1° (compared to the 8.2° twist angle of the corresponding planes in $[(SIPr)Cu(CO)_2][SbF_6]$). This is perhaps a result of a steric effect caused by substituents on nitrogen atoms of the *N*-heterocyclic carbene. As evident from the space-filling models illustrated in Figure 6, 2,6-(*i*-Pr)$_2$C$_6$H$_3$ and 2,6-(Ph$_2$CH)$_2$-4-(Me)C$_6$H$_2$ substituents on nitrogen atoms of the two copper dicarbonyl adducts have crevices with different orientations relative to the *N*-heterocyclic carbene plane that are occupied by $Cu(CO)_2$ moieties.

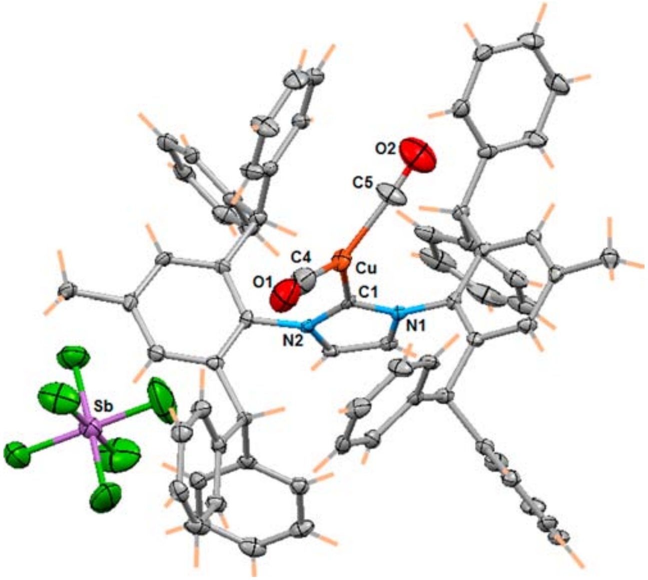


Figure 5. Molecular structure showing $[(IPr^*)Cu(CO)_2][SbF_6]$ (**5**); ellipsoids are shown at the 40% probability level. Selected bond distances (Angstroms) and angles (degrees): Cu−C1 1.947(5), Cu−C4 1.883(7), Cu−C5 1.948(7), O1−C4 1.132(8), O2−C5 1.108(8), N1−C1 1.364(6), N2−C1 1.355(6); C4−Cu−C1 129.7(3), C5−Cu−C1 118.6(3), C4−Cu−C5 110.5(3), O1−C4−Cu 172.2(7), O2−C5−Cu 175.5(8), Cu−C1−N1 126.2(4), Cu−C1−N2 130.0(4).

In summary, we described the synthesis, isolation, and X-ray structural data of two rare copper(I) dicarbonyl complexes. Contrary to the normal belief that weakly coordinating ligands are necessary to stabilize $Cu^I(CO)_2$ moieties,[35] here we show that strongly donating *N*-heterocyclic carbene ligands are also capable of serving as auxiliary ligands for $Cu^I(CO)_2$, as evident from isolable species like $[(SIPr)Cu(CO)_2][SbF_6]$ and $[(IPr^*)Cu(CO)_2][SbF_6]$. They show high CO stretching frequencies (in "nonclassical" metal carbonyl regions), indicating that Cu(I)−CO interaction is dominated by electrostatic and OC → Cu *σ*-donor components. This work also suggests that *N*-heterocyclic carbene ligands are poor charge donors (do not reduce the positive charge on copper significantly).[52] Both $[(IPr^*)Cu(CO)_2][SbF_6]$ and $[(SIPr)Cu(CO)_2][SbF_6]$ are very sensitive to moisture and readily coordinate water at the expense of one of the CO groups, forming the related $[(IPr^*)Cu(CO)(H_2O)][SbF_6]$ and $[(SIPr)Cu(CO)(H_2O)][SbF_6]$. This process however is reversible. Bubbling excess CO through dichloromethane solutions of $[(IPr^*)Cu(CO)(H_2O)][SbF_6]$ and $[(SIPr)Cu(CO)(H_2O)][SbF_6]$ leads to the corresponding dicarbonyl adducts $[(IPr^*)Cu(CO)_2][SbF_6]$ and $[(SIPr)Cu(CO)_2][SbF_6]$. We also reported a rare two-coordinate Cu(I)−aqua complex $[(IPr^*)Cu(H_2O)][SbF_6]$. It can also be converted to $[(IPr^*)Cu(CO)_2][SbF_6]$ by treating with excess CO.

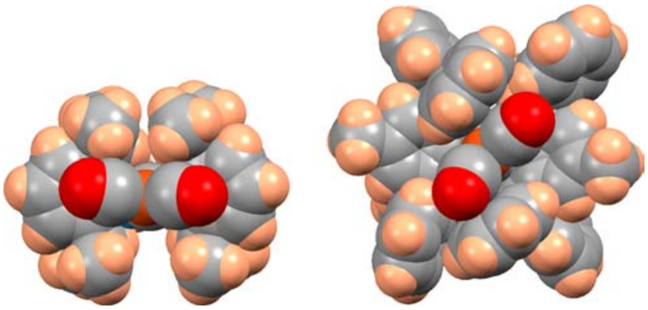


Figure 6. Space-filling models of $[(SIPr)Cu(CO)_2]^+$ (left) and $[(IPr^*)Cu(CO)_2]^+$ (right) showing the orientation of $Cu(CO)_2$ moiety relative to the *N*-heterocyclic carbene plane.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox. Solvents were purchased from commercial sources and purified using an Innovative Technology SPS-400 PureSolv solvent drying system degassed by the freeze−pump−thaw method twice prior to use. Glassware was oven dried at 150 °C overnight. NMR spectra were recorded at 298 K on JEOL Eclipse 500 spectrometer (^{1}H, 500.16 MHz; ^{13}C, 125.77 MHz). Proton and carbon chemical shifts are reported in ppm and referenced using residual proton and carbon signals of the deuterated solvent. NMR annotations used: br = broad, d = doublet, m = multiplet, s = singlet, t = triplet. Infrared spectra were recorded on a JASCO FT-IR 410 spectrometer operating at 2 cm^{-1} spectral resolution. IR spectroscopic data were collected using KBr pellets or mulls between NaCl plates prepared using solid material and Nujol. Herein, we use abbreviations based on IUPAC guidelines, that is, υ for frequency and $\bar{\upsilon}$ for wavenumber. Elemental analyses were performed using a Perkin-Elmer Series II CHNS/O analyzer. $Me_2S\cdot CuBr$ and $AgSbF_6$ were purchased from Sigma-Aldrich and used without further purification. (SIPr)CuBr[53] and IPr*HCl[46] were synthesized using literature procedures.

$[(SIPr)Cu(CO)_2][SbF_6]$. A mixture of (SIPr)CuBr (0.109 g, 0.204 mmol) and $AgSbF_6$ (0.070 g, 0.204 mmol) in dichloromethane (ca. 8 mL) was placed in a 50 mL Schlenk flask. The mixture was saturated with CO by bubbling CO through the solution for about 10 min and stirred for 1 h at −18 °C (using ice/acetone bath). The resulting mixture was filtered through a pad of Celite via canula. The filtrate was again saturated with CO for another 10 min. The solution was layered with hexanes and kept in a refrigerator (−10 °C) under CO atmosphere overnight to obtain colorless prism-shaped crystals of

$[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})_2][\mathrm{SbF}_6]$. The solution was removed using a syringe, and the crystals were separated and dried under a CO stream (0.096 g, 63% yield with respect to copper dicarbonyls). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 7.46 (t, 2H, $^3J_{\mathrm{HH}}$ = 8 Hz, C_6H_3), 7.29 (d, 4H, $^3J_{\mathrm{HH}}$ = 8 Hz, C_6H_3), 4.11 (s, 4H, CH_2), 3.03 (sept, 4H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $CH(\mathrm{CH_3})_2$), 1.35 (d, 12H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{CH}(CH_3)_2$), 1.29 (d, 12H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{CH}(CH_3)_2$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 200.3 (Cu−NCN), 147.1, 134.2, 130.7, 125.2, 54.4 ($\mathrm{NCH_2}$), 29.2 ($C\mathrm{H(CH_3)_2}$), 25.6 ($\mathrm{CH(CH_3)_2}$), 24.1 ($\mathrm{CH(CH_3)_2}$). IR (KBr, selected bands) cm^{-1}: 2168 (CO) m, 2149 (CO) s and additional 2144 and 2133 bands resulting from decomposition products. IR (Nujol mull, selected bands) cm^{-1}: 2167 (CO) m, 2148 (CO) s and additional 2144, 2131 resulting from decomposition products. Anal. Calcd for $\mathrm{C_{29}H_{38}N_2O_2F_6CuSb\cdot0.33CH_2Cl_2}$: C, 45.50; H, 5.03; N, 3.62. Found: C, 45.67; H, 4.80; N, 3.65. $[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})_2][\mathrm{SbF}_6]$ is a colorless solid. It is air and moisture sensitive, often producing monocarbonyl water adduct $[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})(\mathrm{H_2O})][\mathrm{SbF}_6]$ noted below and presumably $[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})][\mathrm{SbF}_6]$. Solid samples kept in a sealed container under an inert atmosphere at −10 °C refrigerator showed $\bar{\upsilon}_{\mathrm{CO}}$ band for dicarbonyl species in the IR spectrum even after 14 days, but $\mathrm{CH_2Cl_2}$ solutions of $[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})_2][\mathrm{SbF}_6]$ lose CO upon concentration under reduced pressure.

$[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})(\mathrm{H_2O})][\mathrm{SbF}_6]$. A mixture of (SIPr)CuBr (0.081 g, 0.152 mmol) and $\mathrm{AgSbF_6}$ (0.052 g, 0.152 mmol) in dichloromethane (ca. 8 mL) was placed in a 50 mL Schlenk flask. The mixture was saturated with CO by bubbling CO through the solution for about 10 min and stirred for 1 h at −18 °C (using ice/acetone bath). The resulting mixture was filtered through a pad of Celite via canula. The filtrate was saturated with $\mathrm{N_2}$ gas for 10 min. The solution was layered with hexanes and kept in a refrigerator (−10 °C) overnight to obtain colorless crystals of $[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})(\mathrm{H_2O})][\mathrm{SbF}_6]$. The solution was removed using a syringe, and crystals were separated and dried using a nitrogen stream (0.061 g, 54% yield). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 7.46 (t, 2H, $^3J_{\mathrm{HH}}$ = 8 Hz, C_6H_3), 7.31 (d, 4H, $^3J_{\mathrm{HH}}$ = 8 Hz, C_6H_3), 4.12 (s, 4H, CH_2), 4.09 (s, 2H, H_2O), 3.04 (sept, 4H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $CH(\mathrm{CH_3})_2$), 1.36 (d, 12H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{CH}(CH_3)_2$), 1.30 (d, 12H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{CH}(CH_3)_2$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 200.2 (Cu−NCN), 147.1, 134.2, 130.7, 125.2, 54.4 ($\mathrm{NCH_2}$), 29.3 ($C\mathrm{H(CH_3)_2}$), 25.7 ($\mathrm{CH(CH_3)_2}$), 24.1 ($\mathrm{CH(CH_3)_2}$). IR (KBr, selected bands) cm^{-1}: 2133 (CO) s. IR (Nujol mull, selected bands) cm^{-1}: 2133 (CO) s. Anal. Calcd for $\mathrm{C_{28}H_{40}N_2O_2F_6CuSb\cdot0.5CH_2Cl_2}$: C, 43.98; H, 5.31; N, 3.60. Found: C, 44.21; H, 5.63; N, 3.61. $[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})(\mathrm{H_2O})][\mathrm{SbF}_6]$ is a colorless solid. IR spectrum of the solid samples showed a $\bar{\upsilon}_{\mathrm{CO}}$ band for carbonyl species even after being stored in a sealed container for several weeks under an inert atmosphere at −30 °C refrigerator, but in $\mathrm{CH_2Cl_2}$ solutions, $[(\mathrm{SIPr})\mathrm{Cu}(\mathrm{CO})(\mathrm{H_2O})][\mathrm{SbF}_6]$ loses CO upon concentration under reduced pressure.

(IPr*)CuBr. A mixture of IPr*HCl (2.13 g, 2.24 mmol) and KO^{t}Bu (0.302 g, 2.69 mmol) in THF (60 mL) was stirred for 30 min at room temperature. $(\mathrm{SMe_2})\mathrm{CuBr}$ (0.461 g, 2.24 mmol) was then added as a solid to it. The resulting mixture was stirred for 8 h. Solvent was removed under vacuum, and crude residue was dissolved in dichloromethane (60 mL). The mixture was filtered through a pad of Celite, and the solvent from filtrate was removed under vacuum to obtain an off-white solid. The solid was washed with hexane (3 × 10 mL) and dried under vacuum to obtain (IPr*)CuBr (1.79 g, 76% yield). Mp: 320 °C (shows signs of decomposition starting at 280 °C). ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 7.18−7.14 (m, 24H, CH_{Ar}), 7.02−7.01 (m, 8H, CH_{Ar}), 6.90−6.89 (m, 8H, CH_{Ar}), 6.84 (s, 4H, CH_{Ar}), 5.85 (s, 2H, $CH_{\mathrm{imidazole}}$), 5.19 (s, 4H, $C\mathrm{HPh_2}$), 2.22 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K): δ 181.2 (Cu−NCN), 143.2 (C_{Ar}), 142.4 (C_{Ar}), 141.0 (C_{Ar}), 140.2 (C_{Ar}), 134.3 (C_{Ar}), 130.3 ($\mathrm{CH_{Ar}}$), 129.7 ($\mathrm{CH_{Ar}}$), 129.5 ($\mathrm{CH_{Ar}}$), 128.8 ($\mathrm{CH_{Ar}}$), 128.5 ($\mathrm{CH_{Ar}}$), 126.8 ($\mathrm{CH_{Ar}}$), 126.7 ($\mathrm{CH_{Ar}}$), 123.4 ($\mathrm{CH_{imidazole}}$), 51.3 ($\mathrm{CHPh_2}$), 22.0 ($\mathrm{CH_3}$). IR (KBr) cm^{-1}: 3164 w, 3139 w, 3083 w, 3058 m, 3024 m, 2963 w, 2921 w, 1951 w, 1886 w, 1809 w, 1734 w, 1700 w, 1653 w, 1599 s, 1582 m, 1559 w, 1494 s, 1474 s, 1446 s, 1406 m, 1385 w, 1326 w, 1261 m, 1220 w, 1181 w, 1153 m, 1077 s, 1030 s, 1003 w, 944 w, 915 w, 883 w, 853 w, 785 w, 767 w, 711 w. Anal. Calcd for $\mathrm{C_{69}H_{56}N_2BrCu\cdot0.33CH_2Cl_2}$: C, 76.75; H, 5.26; N, 2.58. Found: C, 76.95; H, 4.90; N, 2.39.

$[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{CO})_2][\mathrm{SbF}_6]$. A mixture of (IPr*)CuBr (0.101 g, 0.096 mmol) and $\mathrm{AgSbF_6}$ (0.033 g, 0.096 mmol) in dichloromethane (ca. 10 mL) was placed in a 50 mL Schlenk flask. The mixture was saturated with CO by bubbling CO through the solution for about 10 min and stirred for 1 h at −18 °C (using an ice/acetone bath). The resulting mixture was filtered through a pad of Celite via canula. The filtrate was again saturated with CO for another 10 min. The solution was layered with hexanes and kept in a refrigerator (−10 °C) under CO atmosphere overnight to obtain colorless prism-shaped crystals of $[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{CO})_2][\mathrm{SbF}_6]$. The solution was removed using a syringe, and crystals were separated and dried under a CO stream (0.071 g, 58% yield with respect to copper dicarbonyls). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 7.29−7.22 (m, 24H, CH_{Ar}), 6.91−6.90 (m, 12H, CH_{Ar}), 6.85−6.84 (m, 8H, CH_{Ar}), 6.08 (s, 2H, $CH_{\mathrm{imidazole}}$), 5.06 (s, 4H, $C\mathrm{HPh_2}$), 2.25 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 175.6 (Cu−NCN), 142.9 (C_{Ar}), 142.8 (C_{Ar}), 141.1 (C_{Ar}), 140.7 (C_{Ar}), 133.7 (C_{Ar}), 131.1 ($\mathrm{CH_{Ar}}$), 129.7 ($\mathrm{CH_{Ar}}$), 129.6 ($\mathrm{CH_{Ar}}$), 129.5 ($\mathrm{CH_{Ar}}$), 129.2 ($\mathrm{CH_{Ar}}$), 127.7 ($\mathrm{CH_{Ar}}$), 127.6 ($\mathrm{CH_{Ar}}$), 124.8 ($\mathrm{CH_{imidazole}}$), 51.9 ($\mathrm{CHPh_2}$), 21.8 ($\mathrm{CH_3}$). IR (KBr, selected bands) cm^{-1}: 2171 (CO) m, 2151 (CO) s and additional 2143 and 2135 bands resulting from decomposition products. IR (Nujol mull, selected bands) cm^{-1}: 2171 (CO) m, 2151 (CO) s and additional 2144, 2135 bands resulting from decomposition products. Anal. Calcd for $\mathrm{C_{71}H_{56}N_2O_2F_6CuSb\cdot CH_2Cl_2}$: C, 63.89; H, 4.32; N, 2.07. Found: C, 64.15; H, 4.46; N, 2.14. $[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{CO})_2][\mathrm{SbF}_6]$ is a colorless solid that is air and moisture sensitive (often producing monocarbonyl water adduct $[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{CO})(\mathrm{H_2O})][\mathrm{SbF}_6]$ and presumably $[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{CO})][\mathrm{SbF}_6]$). The solid showed a $\bar{\upsilon}_{\mathrm{CO}}$ band for dicarbonyl species in the IR spectrum even after being stored in a sealed container for 7 days under an inert atmosphere at −10 °C in a refrigerator. $\mathrm{CH_2Cl_2}$ solutions of $[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{CO})_2][\mathrm{SbF}_6]$ lose CO upon concentration under reduced pressure.

$[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{H_2O})][\mathrm{SbF}_6]$. A mixture of (IPr*)CuBr (0.151 g, 0.143 mmol) and $\mathrm{AgSbF_6}$ (0.049 g, 0.143 mmol) in dichloromethane (ca. 12 mL) was taken in a 50 mL Schlenk flask. The mixture was stirred for 1 h at 0 °C. The resulting mixture was filtered through a pad of Celite via canula. The filtrate was layered with hexanes and kept in a refrigerator (−10 °C) overnight to obtain colorless prism-shaped crystals of $[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{H_2O})][\mathrm{SbF}_6]$ (0.123 g, 70% yield). ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 7.28−7.25 (m, 16H, CH_{Ar}), 7.22−7.19 (m, 8H, CH_{Ar}), 6.92−6.90 (m, 8H, CH_{Ar}), 6.85 (s, 4H, CH_{Ar}), 6.81−6.79 (m, 8H, CH_{Ar}), 6.01 (s, 2H, $CH_{\mathrm{imidazole}}$), 5.08 (s, 4H, $C\mathrm{HPh_2}$), 3.42 (br, 2H, H_2O), 2.27 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K): δ 175.9 (Cu−NCN), 142.8 (C_{Ar}), 142.2 (C_{Ar}), 140.7 (C_{Ar}), 140.6 (C_{Ar}), 133.6 (C_{Ar}), 130.8 ($\mathrm{CH_{Ar}}$), 130.0 ($\mathrm{CH_{Ar}}$), 129.5 ($\mathrm{CH_{Ar}}$), 129.1 ($\mathrm{CH_{Ar}}$), 128.9 ($\mathrm{CH_{Ar}}$), 127.5 ($\mathrm{CH_{Ar}}$), 127.3 ($\mathrm{CH_{Ar}}$), 124.2 ($\mathrm{CH_{imidazole}}$), 51.5 ($\mathrm{CHPh_2}$), 21.9 ($\mathrm{CH_3}$). IR (KBr) cm^{-1}: 3447 br, 3164 w, 3139 w, 3084 w, 3060 w, 3025 m, 3002 w, 2961 w, 2923 w, 1955 w, 1889 w, 1810 w, 1733 w, 1600 s, 1582 w, 1558 w, 1494 s, 1472 s, 1447 s, 1408 w, 1384, 1332, 1262 s, 1221 w, 1180 w, 1154 w, 1078 s, 1031 s, 1004 w, 944 w, 915 w, 883 w, 854 w, 786 w, 763 w, 746 w, 704 w. Anal. Calcd for $\mathrm{C_{69}H_{58}N_2OF_6CuSb}$: C, 67.35; H, 4.75; N, 2.28. Found: C, 67.03; H, 4.79; N, 2.17. $[(\mathrm{IPr^*})\mathrm{Cu}(\mathrm{H_2O})][\mathrm{SbF}_6]$ is a colorless solid and can be stored in a sealed container under an inert atmosphere for several weeks without decomposition. It is soluble in dichloromethane and chloroform.

X-ray Crystallographic Data. A suitable crystal covered with a layer of paratone-N oil was selected and mounted with in a cryo-loop and immediately placed in the low-temperature nitrogen stream. Diffraction data were collected at T = 100(2) K. Data sets were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data were processed using the Saint Plus program. All calculations for structure determination were carried out using the SHELXTL package (version 6.14).[54] Initial atomic positions were located by direct methods using XS, and structures of the compounds were refined by the least-squares method using XL. Absorption corrections were applied using SADABS. Hydrogen atoms were included at calculated positions and refined in a riding manner along with the attached carbons. Additional details are provided in the cif files.

Crystallographic Data for [(SIPr)Cu(CO)$_2$][SbF$_6$]. Formula = $C_{29}H_{38}N_2O_2F_6CuSb$; fw = 745.90; temp =100(2) K; space group = monoclinic $P2(1)/c$; a = 12.0411(8) Å, b = 15.0609(10) Å, c = 18.7044(11) Å; $\alpha = 90°$, $\beta = 109.714(3)°$, $\gamma = 90°$; V = 3193.2(4) Å^3; Z = 4, density (calcd) = 1.552 Mg/m^3; no of reflns collected = 31 030; no. of independent reflns = 7913 [R(int) = 0.0303]; final R indices [$I > 2\sigma(I)$] R1 = 0.0320, wR2 = 0.0788; R indices (all data) R1 = 0.0375, wR2 = 0.0817.

Crystallographic Data for [(IPr)Cu(CO)$_2$][SbF$_6$]·CH$_2$Cl$_2$.* Formula = $C_{72}H_{58}Cl_2N_2O_2F_6CuSb$; fw = 1353.39; temp = 100(2) K; space group = monoclinic $P2(1)/n$; a = 15.9597(14) Å, b = 17.2197(15) Å, c = 23.051(2) Å; $\alpha = 90°$, $\beta = 106.446(1)°$, $\gamma = 90°$; V = 6075.8(9) Å^3; Z = 4, density (calcd) = 1.480 Mg/m^3; no of reflns collected = 49 963; no. of independent reflns = 11 950 [R(int) = 0.0977]; final R indices [$I > 2\sigma(I)$] R1 = 0.0641, wR2 = 0.1518; R indices (all data) R1 = 0.1273, wR2 = 0.1807.

Crystallographic Data for [(IPr)Cu(H$_2$O)][SbF$_6$]·2CH$_2$Cl$_2$.* Formula = $C_{71}H_{62}Cl_4N_2OF_6CuSb$; fw = 1400.32; temp = 100(2) K; space group = monoclinic $P2(1)/c$; a = 15.5624(16) Å, b = 18.472(2) Å, c = 24.6683(17) Å; $\alpha = 90°$, $\beta = 116.961(4)°$, $\gamma = 90°$; V = 6320.6(10) Å^3; Z = 4, density (calcd) = 1.472 Mg/m^3; no of reflns collected = 62 101; no. of independent reflns = 15 656 [R(int) = 0.0317]; final R indices [$I > 2\sigma(I)$] R1 = 0.0439, wR2 = 0.1149; R indices (all data) R1 = 0.0545, wR2 = 0.1232.

■ ASSOCIATED CONTENT

S Supporting Information

X-ray crystallographic data (CIF) for [(SIPr)Cu(CO)$_2$][SbF$_6$], [(IPr*)Cu(CO)$_2$][SbF$_6$]·CH$_2$Cl$_2$, and [(IPr*)Cu(H$_2$O)]-[SbF$_6$]·2CH$_2$Cl$_2$ and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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