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1,3,5-Tris(thiocyanatomethyl)mesitylene as a Ligand. Pseudooctahedral Molybdenum, Manganese, and Rhenium Carbonyl Complexes and Copper and Silver Dimers. Copper-Catalyzed Carbene- and Nitrene-Transfer Reactions

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New molybdenum(0), molybdenum(II), manganese(I), rhenium(I), silver(I), and copper(I) complexes with the 1,3,5-tris(thiocyanatomethyl)mesitylene [Ms(CH$_2$SCN)$_3$] ligand have been synthesized and characterized by IR, NMR, and by X-ray diffraction (except for the rhenium complex). The Ms(CH$_2$SCN)$_3$ ligand coordinated with the molybdenum, manganese, and rhenium carbonyl fragments as a tripodal chelate. With copper and silver, dimeric dicationic species were obtained instead, with the Ms(CH$_2$SCN)$_3$ ligand acting simultaneously as a bidentate chelate and bridge. The [{Cu(Ms(CH$_2$SCN)$_3$)}$_2$][BAr′$_4$]$_2$ (BAr′$_4$ = tetra(3,5-bis(trifluoromethyl)phenyl)borate) product is an excellent catalyst for cyclopropanation and aziridination of alkenes and cyclopropenation of alkynes by means of carbene- and nitrene-transfer reactions.

Introduction

Tripodal nitrogen-donor ligands such as the anionic tris(pyrazolyl)borates or the neutral tris(pyrazolyl)alkanes have been extensively employed in coordination chemistry and catalysis.[1] When these and related ligands act as ligands, the formation of six-membered rings strongly favors coordination to a single metal center as tripodal tridentates. When the donor groups of polydentate ligands are held together by a polyatomic fragment, instead of by a single bridgehead atom, other coordination modes can become favorable. The possibility that one of these ligands can adopt different coordination modes depending on the nature of the metal center to which it is coordinated increases when the donor groups are linked to the bridgehead group through flexible spacers such as methylene groups. Molecules containing 1,3,5-trimethylbenzene bridgehead groups have been used as ligands and as supramolecular hosts (podands).[2] Using these compounds as ligands often produces bi- or tridimensional networks in which the ligand bridges several metal centers.[3] For the Ms(CH$_2$SCN)$_3$ ligand, conformational flexibility (see Scheme 1) is expected. The preparation of 1,3,5-tris(thiocyanatomethyl)mesitylene [Ms(CH$_2$SCN)$_3$] was reported by Suzuki et al. in 1979.[4] No further chemistry of this compound has been reported since then. We have investigated its properties as a ligand toward midtransition, carbonyl metal centers with a strong preference for a pseudooctahedral geometry and toward coordinatively more flexible copper(I) and silver(I) centers. For the copper(I) derivative, the catalytic activity in carbene- and nitrene-transfer reactions was also investigated. Our findings are discussed in this paper.

Results and Discussion

We have synthesized the Ms(CH$_2$SCN)$_3$ compound by a slight modification of the method reported by Suzuki et al.,[4]

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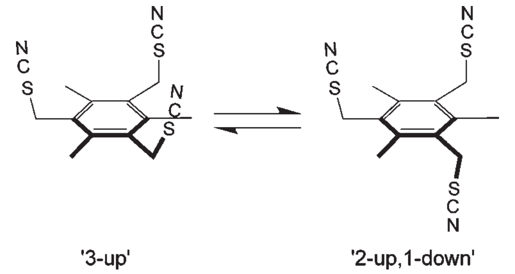
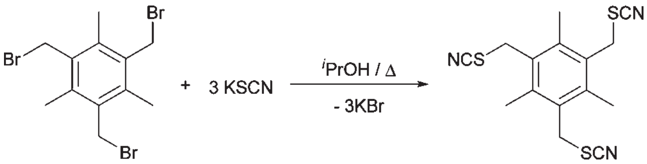
Scheme 1. "Three-Up" and "Two-Up, One-Down" Conformers of $Ms(CH_2SCN)_3$



Scheme 2. Synthesis of $Ms(CH_2SCN)_3$



employing refluxing isopropyl alcohol (^{i}PrOH; instead of *N*,*N*-dimethylformamide) as the solvent, as shown in Scheme 2. A high yield was obtained using a reaction time of 3 h and a stoichiometric amount of potassium thiocyanate (KSCN); therefore, unlike in the original procedure, we did not find it necessary to use an excess of KSCN.

In the IR spectrum of $Ms(CH_2SCN)_3$ in KBr, three ν_{CN} bands were observed at 2159, 2153, and 2140 cm^{-1},[5] while a single band at 2154 cm^{-1} was observed in a CH_2Cl_2 solution. In the ^{1}H NMR spectrum, single signals for both the CH_2 and CH_3 groups were observed. The results of single-crystal X-ray diffraction showed that in the solid state the ligand adopts a "two-up, one-down" conformation (Figure 1).

The N−C−S angles fall between 176.2(4) and 179.0(4)°, indicating sp hybridization of the central carbon, for which two resonance forms can be envisaged (Figure 2).

Organometallic Compounds of Molybdenum, Manganese, and Rhenium

$Ms(CH_2SCN)_3$ was allowed to react with stoichiometric amounts of the labile compounds *fac*-$[Mo(CO)_3(NCMe)_3]$, *fac*-$[Mo(\eta^3\text{-methallyl})(CO)_2(NCMe)_3][BAr'_4]$, *fac*-$[Mn(CO)_3(NCMe)_3][BAr'_4]$, and *fac*-$[Re(CO)_3(NCMe)_3][BAr'_4]$.

In each case, a single product was obtained in high yield, with spectroscopic and analytical data consistent with $[Mo(CO)_3(Ms(CH_2SCN)_3)]$ (**1**), $[Mo(\eta^3\text{-methallyl})(CO)_2(Ms(CH_2SCN)_3)][BAr'_4]$ (**2**), $[Mn(CO)_3(Ms(CH_2SCN)_3)][BAr'_4]$ (**3**), and $[Re(CO)_3(Ms(CH_2SCN)_3)][BAr'_4]$ (**4**) formulation. For the cationic complexes, the same result was obtained either from the preformed tris(nitrile) compound or from the in situ generated compound resulting from the mixing of equimolar amounts of $[MoCl(\eta^3\text{-methallyl})(CO)_2(NCMe)_2]$ or *fac*-$[M(OTf)(CO)_3(NCMe)_2]$ (M = Mn, Re) and $NaBAr'_4$, as indicated in Scheme 3 (see also the Experimental Section). In CH_2Cl_2 solutions, the average of the ν_{CO} bands in the IR spectra is slightly higher than that of the corresponding tris(nitrile) precursors (see Table 1 and the Experimental Section), indicating that the tripodal ligand is slightly less donor than the set of three acetonitriles. This suggests that the higher electronegativity of the SR vis-a-vis the CH_3 group predominates over the electron delocalization of the sulfur lone pairs shown in Figure 2; i.e., the inductive effect predominates over the mesomeric effect. A single, weak ν_{CN} band is observed for each complex. In **2**−**4**, this band occurs at higher frequencies than that in free $Ms(CH_2SCN)_3$ (2154 and 2164 cm^{-1} in **2**, 2196 cm^{-1} in **3**, and 2188 cm^{-1} in **4**), whereas in **1**, it appears at the same frequency as that in $Ms(CH_2SCN)_3$. The shift to higher frequencies of the ν_{CN} band of an NCSR ligand upon coordination, previously observed, has been attributed to some degree of coupling of the C−N and N−M stretching modes.[6]

The NMR spectra of complexes **1**−**4** showed single sets of signals for the CH_2 and CH_3 groups, indicating C_3 symmetry. This is the actual symmetry of the instantaneous structure of the tricarbonyl complexes but not of **2**. Several pseudooctahedral $[Mo(\eta^3\text{-allyl})(CO)_2L_3]$ complexes showed this apparent symmetry in solution because of the operation of dynamic processes that are fast on the NMR time scale at room temperature.[9] To investigate if this is the case for **2**, the ^{1}H NMR spectrum of **2** in CD_2Cl_2 was recorded at different temperatures (Figure 3). At room temperature, the $Ms(CH_2SCN)_3$ ligand featured two broad singlets at 4.49 and 2.49 ppm, corresponding to the CH_2 and CH_3 groups, respectively. Below 10 °C, these signals started to split, and at −20 °C, two distinct singlets for the CH_3 groups are observed at 2.49 and 2.33 ppm, integrating as six and three hydrogen atoms, respectively. At this temperature, the CH_2 groups give rise to a two-hydrogen singlet at 4.42 ppm and two doublets at 3.39 and 4.21 ppm, integrating as two hydrogen atoms each. This pattern indicates the presence of a molecular mirror plane and diastereotopic character of the hydrogen atoms on two of the CH_2 groups. Therefore, an instantaneous C_s-symmetric solution structure similar to the one found in the solid state can be assumed for the cationic complex in **2**. The signals corresponding to the allyl group did not undergo significant changes upon temperature lowering. From the coalescence temperature (282 K), the free energy of activation for the dynamic process can be estimated as $\Delta G^{\ddagger} = 57$ kJ mol^{-1}.[10]

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[8] For IR(ν_{CO}) data of $[M(CO)_3(NCMe)_3]^+$ (M = Mn, Re) with different counteranions (OTf, BPh_4, and PF_6), see:(a) Reimann, R. H.; Singleton, E. *J. Organomet. Chem.* **1973**, *59*, C24. (b) Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 621. (c) Kane-Maguire, L. A. P.; Sweigart, D. A. *Inorg. Chem.* **1979**, *18*, 700. (d) Minutolo, F.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 4514.

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[10] Using a coalescence temperature of 282 K (9 °C) for the δ 2.49 ^{1}H NMR signal [CH_3 of the $Ms(CH_2SCN)_3$ ligand] and a chemical shift difference between the CH_{3a}/CH_{3b} of $\Delta\nu = 66$ Hz and $\Delta G^{\ddagger} = 57$ kJ mol^{-1}, based on $\Delta G^{\ddagger} = RT_c[22.96 + \ln(T_c/\Delta\nu)]$ ($R = 8.31$ J K^{-1}). Considering the data of the couplet diastereotopic CH_2 hydrogen atoms of the $Ms(CH_2SCN)_3$ ligand, δ_A 4.38, δ_B 4.21, and $J_{A-B} = 11.1$ Hz and applying $k_c = \pi[(\nu_A - \nu_B)^2 + 6J_{AB}{}^2]^{1/2}/2^{1/2}$ and $\Delta G^{\ddagger} = RT_c[23.76 - \ln(k_{coal}/T_c)]$ ($R = 8.31$ J K^{-1}), the free energy of activation at the coalescence temperature ($\Delta G^{\ddagger}$) is 55 kJ mol^{-1}. See: *NMR Spectroscopy*, 2nd ed.; Günther, H., Ed. John Wiley & Sons: West Sussex, England, 1995; pp 343 and 355.

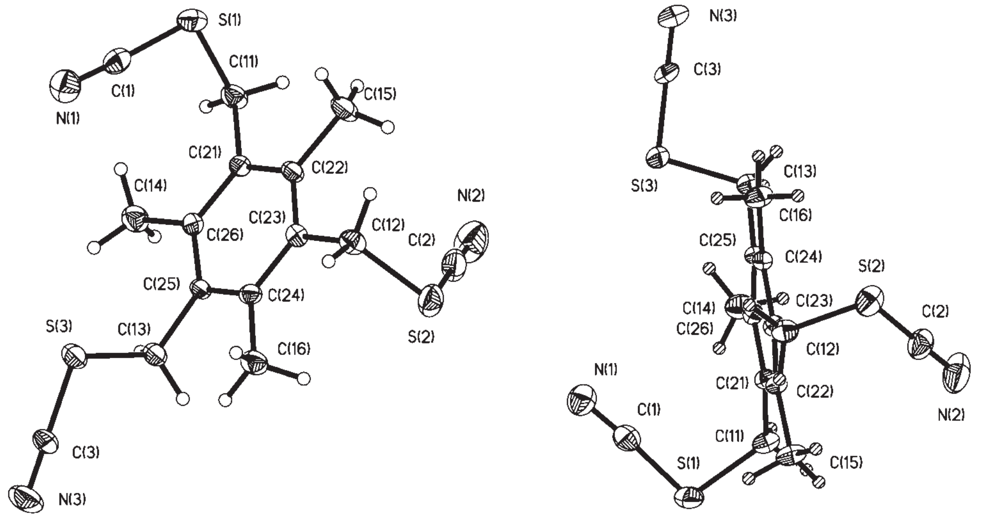


Figure 1. Thermal ellipsoid (30%) plot of $Ms(CH_2SCN)_3$. The view on the right shows the "two-up, one-down" disposition of the CH_2SCN groups. Selected bond distances (Å) and angles (deg): S(1)−C(1) 1.680(5), S(1)−C(11) 1.842(4), S(2)−C(2) 1.676(5), S(2)−C(12) 1.841(4), S(3)−C(3) 1.682(4), S(3)−C(13) 1.828(4), N(1)−C(1) 1.150(5), N(2)−C(2) 1.139(6), N(3)−C(3) 1.141(5); C(1)−S(1)−C(11) 100.26(19), C(2)−S(2)−C(12) 99.5(2), C(3)−S(3)−C(13) 99.70(18), N(1)−C(1)−S(1) 176.2(4), N(2)−C(2)−S(2) 178.6(4), N(3)−C(3)−S(3) 179.0(4), C(21)−C(11)−S(1) 114.4(3), C(23)−C(12)−S(2) 114.9(3), C(25)−C(13)−S(3) 109.0(2).

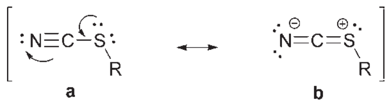


Figure 2. Resonance forms for the RSCN group.

Scheme 3. Synthesis of Carbonyl Compounds of Molybdenum, Manganese, and Rhenium with the $Ms(CH_2SCN)_3$ Ligand

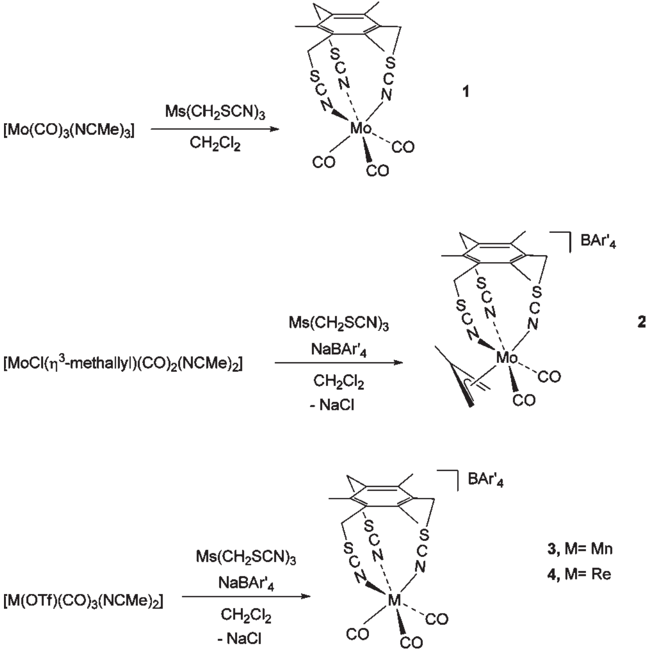
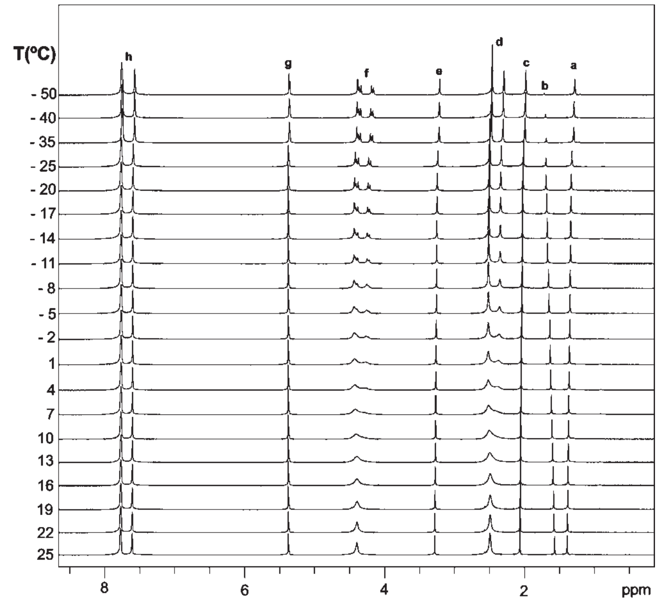


Table 1. IR ν_{CO} (cm^{-1}) in a CH_2Cl_2 Solution

$[Mo(CO)_3(MeCN)_3]$	1922, 1800	**1**	1920, 1840
$[Mo(\eta^3\text{-methallyl})(CO)_2(NCMe)_3][BAr'_4]$7	1974, 1894	**2**	1975, 1904
$[Mn(CO)_3(NCMe)_3][BAr'_4]$8	2068, 1978	**3**	2066, 1985
$[Re(CO)_3(NCMe)_3][BAr'_4]$8	2055, 1952	**4**	2057,1963



a: H_{anti}, **b**: H_2O, **c**: CH_3 (methallyl), **d**: CH_3 ($Ms(CH_2SCN)_3$), **e**: H_{syn}, **f**: CH_2 ($Ms(CH_2SCN)_3$), **g**: CH_2Cl_2, **h**: BAr'_4

Figure 3. VT ^1H NMR of **2** in CD_2Cl_2.

The solid-state structures of compounds **1**−**3** were determined by X-ray crystallography (Figures 4 and 5). The three metal complexes have a pseudooctahedral geometry, with the ligand $Ms(CH_2SCN)_3$ coordinated as *fac* tridentate through the nitrogen atoms. The M−N−C angles are close to linear (average of 177°), indicating the major contribution of the resonance form a (Figure 2). In **2**, the open mouth of the methallyl group points toward the two *cis*-carbonyls, the most energetically favorable arrangement.[11] Neither the angle around the sulfur atom (very close to 100°) nor the H_2C−S, S−C, or C−N distances of the $Ms(CH_2SCN)_3$ ligand undergo a significant distortion by coordination to the metal centers (see Table 2).

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[11] Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

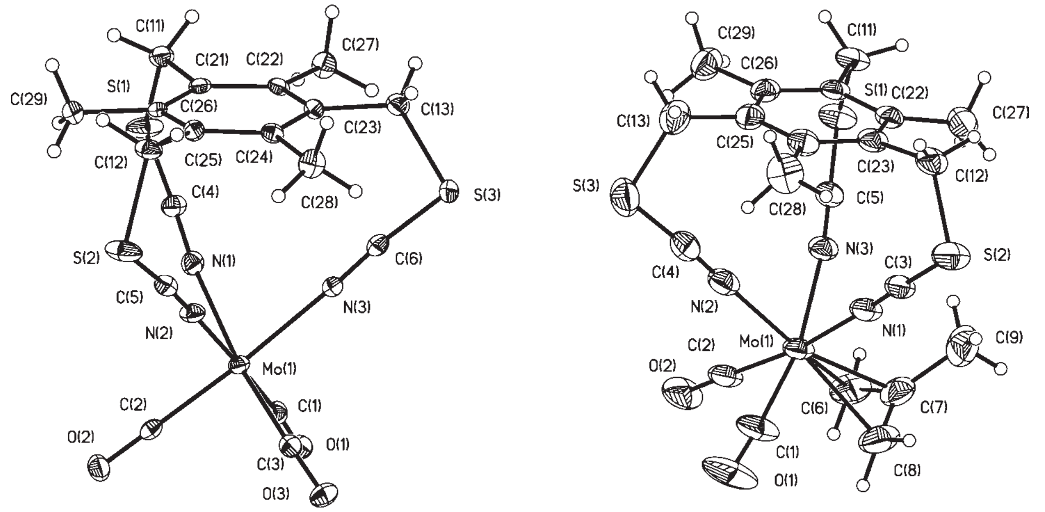

Figure 4. Thermal ellipsoid plot (30% probability) of **1** (left) and the cation in **2**. Selected bond distances (Å) and angles (deg) in **1**: Mo−N(1) 2.219(4), Mo−N(2) 2.194(4), Mo−N(3) 2.211(4), Mo−C(1) 1.951(5), Mo−C(2) 1.954(5), Mo−C(3) 1.949(5), N(1)−C(4) 1.155(6), N(2)−C(5) 1.142(6), N(3)−C(6) 1.150(6), S(1)−C(4) 1.662(5), S(2)−C(5) 1.680(5), S(3)−C(6) 1.677(5); C(4)−N(1)−Mo 172.6(4), C(5)−N(2)−Mo 177.6(4), C(6)−N(3)−Mo 172.4(4), N(2)−Mo−N(3) 82.69(14), N(2)−Mo−N(1) 82.79(14), N(3)−Mo−N(1) 81.17(14), N(1)−C(4)−S(1) 175.2(4), N(2)−C(5)−S(2) 175.8(4), N(3)−C(6)−S(3) 174.8(4), C(4)−S(1)−C(11) 101.9(2), C(5)−S(2)−C(12) 100.7(2), C(6)−S(3)−C(13) 101.1(2). Those in the cation in **2**: Mo−N(1) 2.212(5), Mo−N(2) 2.158(6), Mo−N(3) 2.192(5), Mo−C(6) 2.323(7), Mo−C(7) 2.236(8), Mo−C(8) 2.302(8), Mo−C(1) 1.960(8), Mo−C(2) 1.964(7), N(1)−C(3) 1.129(7), N(2)−C(4) 1.138(8), N(3)−C(5) 1.131(7), S(1)−C(5) 1.668(6), S(2)−C(3) 1.665(7), S(3)−C(4) 1.656(8); N(2)−Mo−N(1) 80.47(19), N(3)−Mo−N(1) 85.09(19), N(2)−Mo−N(3) 80.73(19), C(2)−Mo−N(2) 90.0(3), C(1)−Mo−C(2) 81.7(3), C(3)−N(1)−Mo 177.2(5), C(4)−N(2)−Mo 178.8(5), C(5)−N(3)−Mo 173.3(5), N(1)−C(3)−S(2) 178.1(6), N(2)−C(4)−S(3) 176.3(6), N(3)−C(5)−S(1) 177.0(5), C(5)−S(1)−C(11) 100.3(3), C(3)−S(2)−C(12) 101.1(3), C(4)−S(3)−C(13) 102.3(3).

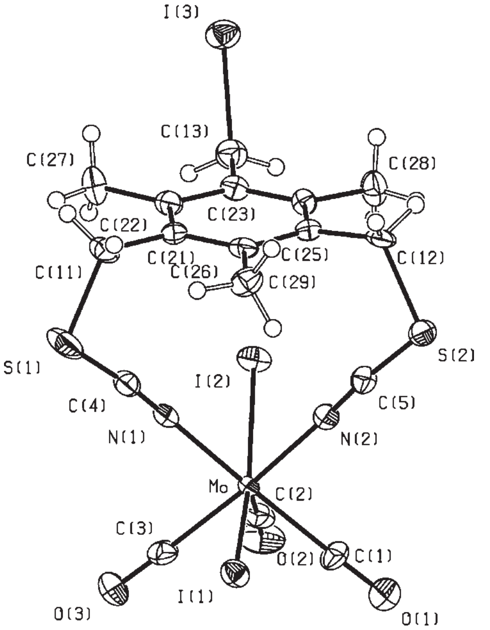

Figure 5. Representative ORTEP (50% probability) of **6**. Selected bond distances (Å) and angles (deg): Mo−I(1) 2.8280(7), Mo−I(2) 2.8786(7), N(1)−Mo 2.187(3), N(2)−Mo 2.183(6), C(1)−Mo 1.998(7), C(2)−Mo 1.983(9), C(3)−Mo 2.005(8), C(4)−N(1) 1.146(11), C(4)−S(1) 1.658(8), C(5)−N(2) 1.162(11), C(5)−S(2) 1.674(8), C(13)−I(3) 2.181(8); N(1)−C(4)−S(1) 174.5(7), N(2)−Mo−N(1) 83.2(2), I(1)−Mo−I(2) 160.94(3), C(4)−N(1)−Mo 169.3(7), C(5)−N(2)−Mo 174.6(6), N(2)−C(5)−S(2) 175.1(7), C(21)−C(11)−S(1) 115.7(5), C(4)−S(1)−C(11) 103.2(4), C(5)−S(2)−C(12) 101.9(4).

As mentioned above, **1** was synthesized by the reaction of $[Mo(CO)_3(NCMe)_3]$ with $Ms(CH_2SCN)_3$ in CH_2Cl_2. Upon standing in an acetonitrile solution for several hours, **1** did not regenerate $[Mo(CO)_3(NCMe)_3]$. This stands in contrast with the behavior reported for $[Mo(Me_3tach)(CO)_3]$ (Me_3tach = 1,3,5-trimethyl-1,3,5-triazacyclohexane),[12] indicating that $Ms(CH_2SCN)_3$ is less labile than Me_3tach. Nevertheless, **1** reacted with KTp* to instantaneously afford $K[MoTp^*(CO)_3]$ [Tp* = hydrotris(3,5-dimethylpyrazolyl)-borate][13] at room temperature. The neutral ligand 2,2′:6,2″-terpyridine (terpy) also displaces $Ms(CH_2SCN)_3$ from **1** at room temperature in CH_2Cl_2; in this case, IR monitoring of the reaction indicated the formation of $[Mo(CO)_4(terpy)]$[14] as the only CO-containing species in solution. The product of this reaction, a decomposition as a tetracarbonyl is produced from a tricarbonyl, is not surprising because $[Mo(CO)_4(terpy)]$ is also the product of the reaction of terpy with $[Mo(CO)_6]$.[14]

Table 2. Average Bond Distances (Å) and C−S−C Angles (deg) of Free and Complexed $Ms(CH_2SCN)_3$

compound	d_{H_2C-S} (Å)	d_{S-CN} (Å)	d_{C-N} (Å)	.
$Ms(CH_2SCN)_3$	1.835(4)	1.679(5)	1.140(6)	99.5(2)
1	1.872(5)	1.671(5)	1.148(6)	100.7(2)
2	1.839(6)	1.662(8)	1.133(7)	101.1(3)
3	1.856(8)	1.689(7)	1.145(9)	101.2(3)

When the equimolar amount of iodine was added to a dichloromethane solution of **1**, a large shift to higher wavenumber values of the ν_{CO} bands in the IR spectrum occurred, indicating the oxidation of molybdenum. The ν_{CO} bands (2034vs, 1966s, and 1943sh cm^{-1}) of the product are very close to those of the previously known complex $[MoI_2(NCMe)_2(CO)_3]$ (2038, 1968, and 1940 cm^{-1}), the product of the reaction of $[Mo(NCMe)_3(CO)_3]$ with iodine.[15] The ^1H NMR spectrum of the product (the reaction crude when the

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[13] Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588.

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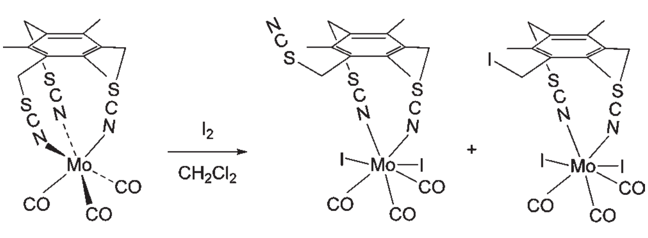
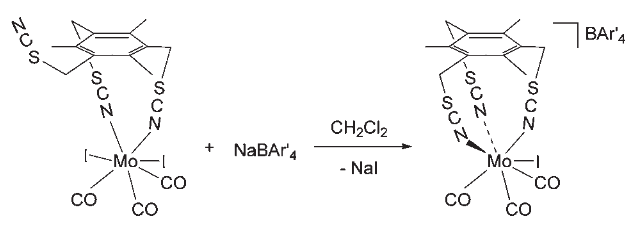
[15] Baker, P. K.; Frases, S. G.; Keys, E. M. *J. Organomet. Chem.* **1986**, *309*, 319.

Scheme 4. Proposed Oxidative Addition of I_2 to **1**



1 **5** **6**

Scheme 5. Proposed Reaction of **5** with $NaBAr'_4$



5 **7**

reaction was carried out in CD_2Cl_2 in an NMR tube) showed it to be a mixture of two compounds, **5** and **6**, in a 2:3 approximate ratio. The solubility of both compounds in dichloromethane and in most common organic solvents was found to be low, as is typical of $[MoI_2(CO)_3L_2]$ complexes.[16] However, the higher solubility of **6** in CH_2Cl_2 made the separation of **5** and **6** possible (see the Experimental Section). The IR ν_{CO} bands of **5** and **6** are identical, reflecting the close similarity between the sets of ligands in both compounds. The nature of compound **6** was unambiguously established by a single-crystal X-ray determination of its structure, the results of which are shown in Figure 5. The molecule of **6** consists of a $MoI_2(CO)_3$ fragment, similar to the ones encountered in previously reported $[MoI_2(CO)_3L_2]$ complexes, coordinated to the nitrogen atoms of the two CH_2SCN groups of an iodomethylbis(thiocyanatomethyl)mesitylene ligand, formally resulting from the substitution by iodide of one of the three SCN groups present in the tridentate ligand of **1**. The ^1H NMR spectrum of **6** in CD_2Cl_2 indicates the presence of a molecular mirror plane, in accordance with the solid-state structure. Thus, there are two singlets at 2.53 and 2.46 ppm, with integrals in a 1:2 ratio, that correspond to the methyl groups. A two-hydrogen singlet at 4.53 ppm and two doublets (two hydrogen atoms each) at 4.69 and 4.21 ppm are assigned to the methylene groups. In the molecule represented in Figure 5, the mirror plane [passing through C(23), C(26), I(2), Mo, I(1), C(2), and O(2)] would make the two CH_2I hydrogen atoms equivalent, while the two hydrogen atoms of each CH_2SCN group are diastereotopic, in accordance with the ^1H NMR spectrum described above. In the ^{13}C NMR spectrum (CD_2Cl_2), two different methyl groups and four different signals for the carbon atoms of the aromatic ring are observed, in agreement with the solid-state structure. However, only one signal is observed for the three carbonyl ligands, and only one signal is seen for the methylene groups probably because of the operation of a fast dynamic process, as is commonly encountered in heptacoordinated halocarbonyl complexes of molybdenum(II).[17]

On the basis of the similarity between the IR spectra (ν_{CO} region) of **5** and **6** and the ^1H NMR spectra discussed below, the structure depicted in Scheme 4 can be proposed for **5**. At room temperature, the ^1H NMR spectrum of **5** in $(CD_3)_2CO$ features single, broad signals for the CH_2 (4.62 ppm) and CH_3 (2.32 ppm) groups. At 0 °C, the CH_2 signal becomes a multiplet and that of CH_3 remains a singlet.

The reaction of **5** with an equimolar amount of $NaBAr_4'$ led to a large shift to higher frequencies in the ν_{CO} bands (2062vs, 2006vs, and 1984 m cm^{-1}), reflecting the formation of a cationic complex **7**. We propose that the third thiocyanate group, free in **5**, coordinated the metal, substituting one of the iodide atoms (see Scheme 5) so that $Ms(CH_2SCN)_3$ is coordinated in a tripodal fashion in the product **7**. Compound **7** is also fluxional because only single signals appear for the CH_2 (4.48 ppm) and CH_3 (2.54 ppm) groups. The solubility of **7** in organic solvents of moderate polarity (e.g., CH_2Cl_2) is larger than those of **5** and **6**, as expected for a BAr'_4 salt. Its ^{13}C NMR spectrum shows a single CO signal at 225.6 ppm. Lowering the temperature down to -60 °C (below this, precipitation occurred) only caused a slight broadening of the signals, a fact that suggests that the dynamic process is still operative at this temperature. Whereas a CH_2Cl_2 solution of **7** is quite stable under a dinitrogen atmosphere, solutions of tetrahydrofuran (THF), diethyl ether, or acetone decompose quickly by a decarbonylation process because the product did not show ν_{CO} bands in the IR spectrum.

Copper and Silver Compounds

Copper (**8**) and silver (**9**) complexes of $Ms(CH_2SCN)_3$ were prepared by a stoichiometric reaction of the ligand with CuOTf or AgOTf and $NaBAr'_4$, as described in the Experimental Section and shown in Scheme 6.

In each case, a single product is obtained in almost quantitative yield. The IR spectrum in a CH_2Cl_2 solution showed a ν_{CN} band at 2174 cm^{-1} for **8** and at 2168 cm^{-1} for **9**, which split into two bands in KBr at 2189 and 2144 cm^{-1} for **8** and at 2191 and 2150 cm^{-1} for **9**.

The ^1H NMR spectra of **8** and **9** showed a 1:1 ratio of $Ms(CH_2SCN)_3/BAr'_4$. For the $Ms(CH_2SCN)_3$ ligand, single sets of signals for the CH_2 and CH_3 groups were observed. The variable-temperature (VT) ^1H NMR spectra of **8** showed that the CH_2 and CH_3 signals broadened and slightly shifted upfield when the temperature was raised to 203 K (see the Supporting Information), but no splitting was observed.

The solid-state structures of **8** and **9** were determined by single-crystal X-ray diffraction. Each compound is a salt consisting of a dicationic complex and two BAr'_4 anions. The copper and silver dicationic complexes are isostructural, centrosymmetric $[M_2\{Ms(CH_2SCN)_3\}]^{2+}$ dimers (see Figure 6). A neutral $[HBpz_3Cu]_2$ species with a structure similar to that found in **8** had been previously described by Marks and coworkers.[18] Each dicationic complex consists of two M^+ metal centers bridged by two $Ms(CH_2SCN)_3$ ligands. One NCSR group of each $Ms(CH_2SCN)_3$ ligand acts as a nitrogen bridge between both metal centers, whereas the other two NCSR groups act as terminal ligands, one to each metal. As a result, each metal atom is tetracoordinated. The four atoms of the

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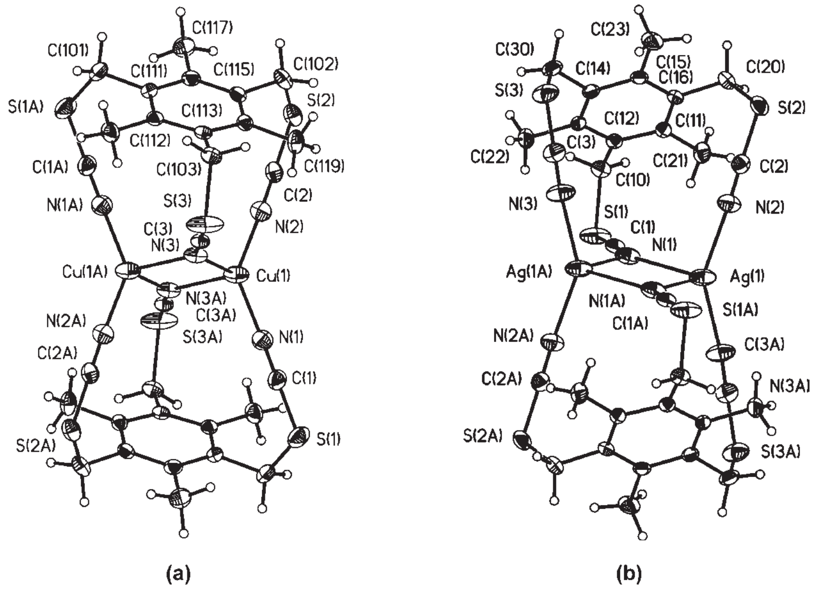

Figure 6. Thermal ellipsoid (30%) plots of the cations in **8** (a) and **9** (b). Selected bond distances (Å) and angles (deg) for the cation in **8**: Cu(1)−N(1) 1.896(4), Cu(1)−N(2) 1.911(4), Cu(1)−N(3) 2.158(4), Cu(1)−N(3) 12.275(4), S(1)−C(1) 1.669(5), S(1)−C(101a) 1.854(5), C(1)−N(1) 1.151(6), S(2)−C(2) 1.675(5), C(2)−N(2) 1.139(6), S(3)−C(3) 1.647(4) C(3)−N(3) 1.139(5), N(3)−Cu(1a) 2.275(4); N(1)−Cu(1)−N(2) 136.47(19), N(1)−Cu(1)−N(3) 108.52(17), N(2)−Cu(1)−N(3) 102.23(15), N(1)−Cu(1)−N(3a) 100.83(15), N(2)−Cu(1)−N(3a) 105.17(16), N(3)−Cu(1)−N(3a) 97.11(13), N(1)−Cu(1)−Cu(1a) 112.28(14), N(2)−Cu(1)−Cu(1a) 111.01(13), N(3)−Cu(1)−Cu(1a) 50.27(11), N(3a)−Cu(1)−Cu(1a) 46.84(10), C(1)−S(1)−C(101a) 100.3(2), N(1)−C(1)−S(1) 177.9(5), C(1)−N(1)−Cu(1) 176.3(5), C(2)−S(2)−C(102) 100.8(2), N(2)−C(2)−S(2) 177.3(4), C(2)−N(2)−Cu(1) 175.7(4). Selected bond distances (Å) and angles (deg) for the cation in **9**: Ag(1)−N(1) 2.490(5), Ag(1)−N(1a) 2.525(5), Ag(1)−N(2) 2.155(5), Ag(1)−N(3a) 2.153(5), C(3)−N(3) 1.135(8), C(2)−N(2) 1.130(7), C(1)−N(1) 1.132(7), C(2)−S(2) 1.682(6), C(3)−S(3) 1.675(6), C(1)−S(1) 1.659(5); N(3A)−Ag(1)−N(2) 145.8(2), N(3A)−Ag(1)−N(1) 110.8(2), N(2)−Ag(1)−N(1) 93.50(17), N(3A)−Ag(1)−N(1A) 95.64(18), N(2)−Ag(1)−N(1A) 108.13(18), N(1)−Ag(1)−N(1A) 90.78(15), C(1)−N(1)−Ag(1) 141.3(5), C(1)−N(1)−Ag(1A) 129.4(5), Ag(1)−N(1)−Ag(1A) 89.22(15), C(2)−N(2)−Ag(1) 176.6(5), C(3)−N(3)−Ag(1A) 174.8(6), N(1)−C(1)−S(1) 175.9(5), N(2)−C(2)−S(2) 176.6(5), N(3)−C(3)−S(3) 178.9(6), C(1)−S(1)−C(10) 103.1(2), C(2)−S(2)−C(20) 100.4(2), C(3)−S(3)−C(30) 100.2(3).

Scheme 6. Synthesis of **8** and **9**

$$[\mathrm{Cu(OTf)}]_2\cdot\mathrm{C_6H_6} \quad + \quad 2\ \mathrm{Ms(CH_2SCN)_3} \xrightarrow[\text{2) 2NaBAr'}_4\text{/ CH}_2\text{Cl}_2]{\text{1) THF/MeCN}} \underset{\mathbf{8}}{[\mathrm{Cu(Ms(CH_2SCN)_3)}][\mathrm{BAr'_4}]}$$

$$\mathrm{AgOTf} \quad + \quad \mathrm{Ms(CH_2SCN)_3} \quad + \quad \mathrm{NaBAr'_4} \xrightarrow[\mathrm{CH_2Cl_2}]{} \underset{\mathbf{9}}{[\mathrm{Ag(Ms(CH_2SCN)_3)}][\mathrm{BAr'_4}]}$$

$M_2N_{2\text{bridge}}$ unit are in a plane, with an almost ideal square geometry in **9** [Ag−N−Ag 89.2(1) and N−Ag−N 90.8(1)°], while **8** shows a significant rhombic distortion [Cu−N−Cu 82.9(1) and N−Cu−N 97.5(1)°]. For the terminal NCSR groups, the N−M−N angles are wider than those of the bridging groups [136.5(5)° in **8** and 145.8(2)° in **9**]. The distances $M-N_{\text{terminal}}$ [1.894(4) and 1.911(4) Å in **8** and 2.155(5) and 2.153(5) Å in **9**] are shorter than $M-N_{\text{bridge}}$ [2.158(4) and 2.275(4) Å in **6** and 2.490(5) and 2.525(5) Å in **9**]. The $Ag-N_{\text{bridge}}$ bond lengths are slightly longer than those in the only known silver complex with a nitrile bridge (2.383(4) and 2.467(4) Å),[19] as expected because in that case each silver atom is tricoordinated, whereas in **9**, it is tetracoordinated.

The $Cu-N_{\text{terminal}}$ distances in **8** [1.894(4) and 1.911(4) Å] are only slightly longer than those found in tetracoordinated copper(I) complexes with the anionic *N*-thiocyanate ligand (1.841−1.985 Å)[20] and shorter than typical $Cu^{I}-N$(nitrile) distances.[21] As discussed above, **8** has two NCSR groups acting as bridges between the copper atoms; to the best of our knowledge, there are no examples of a nitrile nitrogen bridge between two copper atoms and only a few examples with other metals.[20,22] The bridging coordination of one of the NCS groups in **8** and **9** suggests a significant contribution of the resonance form depicted in Figure 2b in the copper and silver complexes. The N−C [average of 1.135(7) Å in **9** and 1.143(6) Å in **8**] and C−S [average of 1.663(5) Å in **9** and 1.663(6) Å in **8**] bond lengths are similar to the distances

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[21] The Cambridge Structural Database (2007) gives a copper−nitrile distance average of 2.040 Å. In the compound $[\mathrm{Cu(NCMe)_4}][\mathrm{B(C_6F_5)_4}]$, the copper−nitrile distances are between 2.000(2) and 2.029(2) Å. See: Zhang, Y.; Sun, W.; Freund, C.; Santos, A. M.; Herdtweck, E.; Mink, J.; Kühn, F. E. *Inorg. Chim. Acta* **2006**, *359*, 4723.

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found in complexes of the anionic thiocyanate ligand.[23] In each complex, the N–C and C–S distances are similar for terminal and bridge groups. As described above for compounds **1**–**3**, the angle around the sulfur atom (100°) does not undergo distortion upon Ms(CH$_2$SCN)$_3$ coordination.

In **9**, the Ag–Ag distance [3.522(1) Å] is too large to be considered as indicative of argentophilic interactions.[24] The Cu–Cu distance in **8** is 2.936(2) Å. In some copper(I) complexes, Cu–Cu interactions (cuprophilic interactions) have been proposed,[25] but they are weaker than the well-established aurophilic interactions.[26] Schwerdtfeger et al. mentioned that the shortest Cu–Cu distances found were 235 pm in tris[1,5-ditolylpentaazadienidocopper(I)],[27] which is shorter than that in the metal (256 pm). A longer Cu–Cu distance, considered as cuprophilic, was found in [Cu$_2$(ophen)$_2$] (Hophen = 2-hydroxy-1,10-phenanthroline), 3.596 Å.[28] All compounds for which cuprophilic interactions have been proposed have an anionic ligand, such as alkyl or halide. In contrast, **8** has only neutral ligands, so that Cu–Cu repulsions due to the noncompensated positive charge on each metal atom should exist. Therefore, the relatively short Cu–Cu distance of 2.936(2) Å could be indicative of some Cu–Cu stabilizing interaction. Such an interaction could be partly responsible for the formation of the dimeric structure of **8** instead of a monomeric complex, with the Ms(CH$_2$SCN)$_3$ ligand acting as a tripodal tridentate. The latter is the geometry most often encountered in tetracoordinated copper(I) complexes with N-tridentate ligands, such as tris(pyrazolyl)borates and tris(pyrazolyl)alkanes,[29] and the structures of compounds **1**–**4** demonstrate that Ms(CH$_2$SCN)$_3$ is able to coordinate a metal center in a tripodal mode. Tridentate coordination is also found in the [(TriMIm)Cu]BF$_4$ complex (Figure 7), where the copper(I) atom is in a trigonal-planar geometry and the ligand has a mesitylene core as the bridgehead group.[30]

Many copper complexes with the thiocyanate (SCN) ligand are known;[20] however, to the best of our knowledge, **8** is the first example of a copper complex with an alkylthiocyanate ligand.

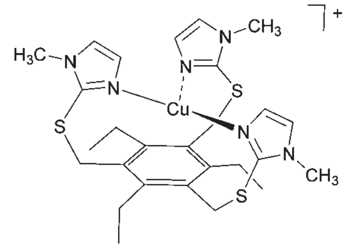

Figure 7. Structure of the [(TriMIm)Cu]$^+$ complex in its tetrafluoroborate salt.

Catalytic Carbene- and Nitrene-Transfer Reactions

We have found that [Cu(TpN)(THF)]$_2$[BAr'$_4$]$_2$ [TpN = tris(2-pyridyl)amine] is an efficient catalyst for carbene- and nitrene-transfer reactions.[31] These results prompted us to test the catalytic activity of **8** in carbene- and nitrene-transfer reactions to olefins (Scheme 7) and carbene transfer to alkynes (Scheme 8). No catalytic activity could be found for the silver complex. Ethyldiazoacetate (EDA) and PhI=NTs were employed as sources of carbene and nitrene groups, respectively.

The reactions were carried out at room temperature in dichloromethane. In cyclopropanation, when EDA was added in one portion to a solution of styrene (5:1 styrene/EDA) in CH$_2$Cl$_2$ in the presence of **8** as the catalyst (1 mol Cu %), a ^{1}H NMR spectrum taken 2 h latter showed a quantitative EDA conversion into a mixture of the two diasteromers of [(2-phenylethoxy)carbonyl]cyclopropane (87%; Table 3) and the olefins resulting from formal carbene dimerization, namely, diethylfumarate and diethylmaleate. When EDA was slowly added over 5 h, formation of the carbene dimers was avoided and cyclopropanation was found to be quantitative. With the other olefins employed, the yields of cyclopropanes obtained reflect their relative reactivity.[32] The results are collected in Table 3.

The color of the final solution was yellow, and no green or blue color, indicative of copper(II) species, was observed.

Complexes with nitrile ligands have been largely used in carbene and nitrene catalytic reactions, mainly because of the lability of nitriles, which provide a vacant coordination site necessary for the formation of the carbene or nitrene intermediate.[29b,31,33] However, nitrilecopper complexes could be unstable, limiting the life of the catalyst. Because the Ms(CH$_2$SCN)$_3$ ligand can be regarded, as a first approach, as a tris(nitrile) ligand, we tested the stability of **8** under the reaction conditions. Thus, we carried out a cyclopropanation experiment with a 5:1 styrene/EDA ratio, 1 mol % of **8** (relative to EDA), and EDA addition over 2 h using a syringe pump. After complete EDA addition, an aliquot was taken and analyzed by ^{1}H NMR spectroscopy, showing quantitative cyclopropanation (100 turnovers). To the reaction

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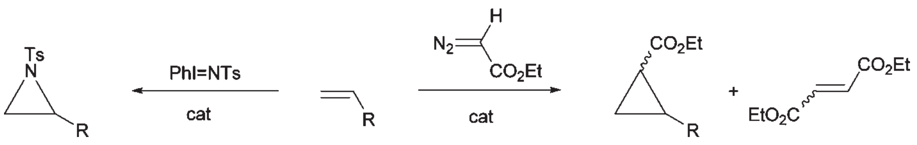
Scheme 7. Cyclopropanation and Aziridination of Olefins



Scheme 8. Catalytic Synthesis of Cyclopropenes

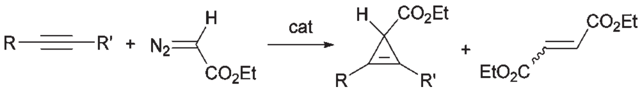


Table 3. Yields of Cyclopropanes and Aziridines in the Copper-Catalyzed Reactions of EDA with Olefins

olefin	% cyclopropanes[a]	% aziridines[e]
styrene	87 (70:17)[b]	
styrene	99 (78:21)[c]	90
1-hexene	35[d]	28
cyclooctene	92[d]	90
cis-stilbene	82 (57:25)[d]	27
trans-stilbene	47[d]	13
1,1-diphenylethylene	90[d]	40

[a] Standard conditions: 5 mmol of substrate, 1 mmol of EDA, 1 mol % **8**, and CH$_2$Cl$_2$ (20 mL). In parentheses, ratio of the trans/cis products. Yield based on EDA and determined by ^{1}H NMR spectroscopy, average of two runs. Mass balance accounted for by diethylmaleate and diethylfumarate formation. [b] EDA added over 0 h. [c] EDA added over 5 h. [d] EDA added over 10 h. [e] Reactions run for 5 h with 5 mmol of substrate, 1 mmol of PhI=NTs, 2 mol % **8**, CH$_2$Cl$_2$ (15 mL). Yield based on PhI=NTs and determined by ^{1}H NMR spectroscopy, average of two runs.

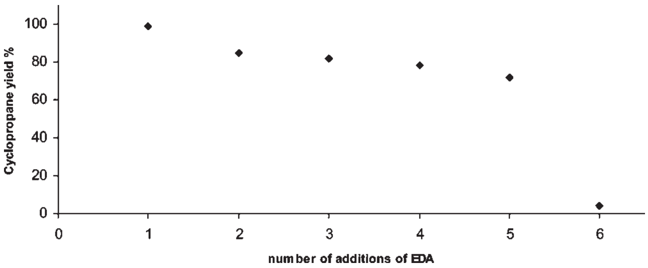


Figure 8. Study of the stability of **8** in the reaction conditions. Each point is the average of two experiments.

Table 4. Cyclopropenation of Alkenes Catalyzed by **8**[a]

substrate	% cyclopropene
phenylacetylene	46
diphenylacetylene	53
1-hexyne	32
3-hexyne	53
1-phenyl-1-propyne	51
ethyl propiolate	42

[a] Standard conditions: 5 mmol of substrate, 1 mmol of EDA (added over 11 h), 1 mol % **8**, CH$_2$Cl$_2$. Yield based on EDA and determined by ^{1}H NMR spectroscopy, average of two runs. Mass balance accounted for by diethylmaleate and diethylfumarate formation.

crude, 100 more equiv of EDA was added over 2 h, and the solution was analyzed by ^{1}H NMR. The EDA addition and the immediate ^{1}H NMR analysis were repeated a total of six times. Figure 8 represents the total cyclopropane yield obtained after each EDA addition.

As can be seen, there is a small yield decrease after each EDA addition. Note that no additional styrene was added for each new addition of EDA. Therefore, in the points shown in Figure 8, the styrene/EDA ratios are 5:1 (as in the cyclopropanation reactions described above), 4:1, 3:1, 2:1, 1:1, and, finally, 0:1. In the final point, the ^{1}H NMR spectrum showed the presence of diethylfumarate and diethylmaleate as major products, reflecting the catalytic activity of **8**, even in the absence of styrene.

We studied the activity of **8** as a catalyst in aziridination reactions (Table 3) using the same olefins as those in cyclopropanation (see above) and PhI=NTs as the nitrene source. The aziridination reactions took place in 5 h, at which time the solution became clear; i.e., PhI=NTs was completely dissolved. The solution immediately changed to a green color after PhI=NTs addition, suggesting the formation of copper(II) species, which could be the resting state of the catalyst.

Compound **8** was employed as a catalyst in cyclopropenation reactions (Scheme 8), and the results are shown in Table 4.

The yields obtained are clearly inferior to those obtained in the cyclopropanation and aziridination reactions, a fact generally encountered when the three reactions employing the same catalyst are compared. The results obtained using **8** as catalysts for cyclopropanation, aziridination, and cyclopropenation showed this new copper compound to be a highly active catalyst.[31,34]

The generation of a catalytic active species could require a Cu–N bond scission to generate a coordination site necessary for the formation of the carbene or nitrene intermediate. The Cu–N$_{\text{bridge}}$ bond is longer and, presumably, weaker than the Cu–N$_{\text{terminal}}$ [d(Cu–N$_{\text{bridge}}$) = 2.158(4) and 2.275(4) Å; d(Cu–N$_{\text{terminal}}$) = 1.894(4) and 1.911(4) Å].[35] Therefore, the cleavage of the bridge could create the open position required for catalytic activity. On the other hand, we do not rule out the possibility that in solution the active catalyst was a mononuclear species, such as that found in the [Cu(TpN)(THF)]$_2$[BAr'$_4$]$_2$ complex.[31]

The tris(thiocyanato) Ms(CH$_2$SCN)$_3$ ligand is special because, being neutral (and, therefore, each copper center is cationic; note that high electrophilicity is considered to be a desirable feature for copper-catalyzed carbene- and nitrene-transfer reactions),[33d] it is able to form a nitrogen bridge between two copper atoms, with long Cu–N distances, presumably indicative of weak Cu–N bonds that would facilitate the creation of empty sites at metal as discussed above. This combination of features could be responsible for the high activity of **8** as the catalyst.

Conclusions

Ms(CH$_2$SCN)$_3$ is a versatile ligand that can act as a *fac* tripodal tridentate in molybdenum(0), molybdenum(II),

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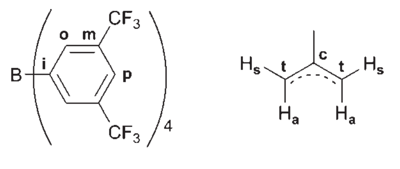
manganese(I), and rhenium(I) complexes or as a bidentate chelate and a bridge in copper(I) and silver(I) compounds. This ligand did not need distortion for both types of coordination, with the angle about sulfur remaining 100° upon coordination. For pseudooctahedral complexes, the close to linear M−N−C angles indicate the predominance of the resonance form a (see Figure 2), whereas in the bridging groups of the copper and silver complexes, the lower angles reflect the major contribution of form b. The dimeric copper complex **8** is an efficient catalyst for carbene- and nitrene-transfer reactions to afford cyclopropanes, cyclopropenes, and aziridines.

Experimental Section

All manipulations were carried out at room temperature under a dinitrogen atmosphere employing Schlenk techniques. ^{i}PrOH (technical grade) was used as received (the same results were obtained by employing pure ^{i}PrOH distilled under a dinitrogen atmosphere), and CH_2Cl_2 was dried over CaH_2, THF over sodium benzophenone, and hexane over sodium. IR and NMR spectra were recorded on Perkin-Elmer FT1720-X and Bruker AV-400 spectrometers, respectively. Deuterated solvents were degassed by three freeze−pump−thaw cycles, dried over 4 Å molecular sieves, and stored in the dark. EDA was added using a Cole Parmer (74900 series) syringe pump and a Hamilton gastight 20 mL syringe. $[Mo(CO)_3(NCMe)_3]$,[36] $[MoCl(\eta^3\text{-methallyl})(CO)_2(NCMe)_2]$,[37] $[MnBr(CO)_5]$,[38] $[ReBr(CO)_3(NCMe)_2]$,[39] $NaBAr'_4$,[40] and PhI=NTs (stored at −20 °C under a dinitrogen atmosphere)[41] were prepared according to literature procedures. All other chemicals were purchased and used without further purification.



Labeling scheme for BAr'$_4$ and methallyl

1,3,5-Tris(thiocyanatomethyl)mesitylene [Ms(CH$_2$SCN)$_3$]. A mixture of 1,3,5-tris(bromomethyl)mesitylene (0.500 g, 1.253 mmol) and KSCN (0.393 g, 4.010 mmol) in ^{i}PrOH (20 mL) was refluxed for 3 h. After reaching room temperature, the solution was allowed to settle, and the white solid was redissolved in CH_2Cl_2 and filtered through diatomaceous earth. In vacuo concentration to 10 mL and the addition of hexane (20 mL) caused the precipitation of a microcrystalline white solid, which was washed with hexane and dried under vacuum. Colorless crystals of X-ray quality were obtained by the slow diffusion of hexane into a concentrated solution of $Ms(CH_2SCN)_3$ in CH_2Cl_2 at −20 °C. Yield: 0.387 g, 92%. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2154. IR (KBr, cm^{-1}): ν_{CN} 2158, 2153, 2140. ^{1}H NMR ($CDCl_3$): δ 4.43 [s, 6H, CH_2SCN], 2.53 [s, 9H, CH_3].

[Mo(CO)$_3$(Ms(CH$_2$SCN)$_3$)] (1). To a solution of freshly prepared $[Mo(CO)_3(NCMe)_3]$ (0.230 mmol) in CH_2Cl_2 (10 mL) was slowly added a solution of $Ms(CH_2SCN)_3$ (0.076 g, 0.230 mmol) in CH_2Cl_2 (20 mL). Immediately, yellow crystals of **1** were formed, one of which was used for X-ray analysis. Yield: 0.075 g, 63%. Anal. Calcd. for $C_{18}H_{15}MoN_3O_3S_3$: C, 42.11; H, 2.94; N, 8.18. Found: C, 42.35; H, 3.21; N, 7.91. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2155 w, ν_{CO} 1920 vs, 1813 s. ^{1}H NMR (CD_3CN): δ 4.48 [s, 6H, CH_2SCN], 2.50 [s, 9H, CH_3].

[Mo(η^3-methallyl)(CO)$_2$(Ms(CH$_2$SCN)$_3$)][BAr'$_4$] (2). To a solution of $[MoCl(\eta^3\text{-methallyl})(CO)_2(NCMe)_2]$ (0.030 g, 0.090 mmol) in CH_2Cl_2 (10 mL) were added $NaBAr'_4$ (0.079 g, 0.090 mmol) and $Ms(CH_2SCN)_3$ (0.031 g, 0.090 mmol), and the mixture was stirred for 15 min. After filtration through diatomaceous earth and in vacuo concentration, the yellow solution was layered with hexane (10 mL) and placed at −20 °C, affording yellow crystals, one of which was used for the structure determination by X-ray diffraction. Yield: 0.112 g, 94%. Anal. Calcd for $C_{53}H_{34}BF_{24}MoN_3O_3S_3\cdot CH_2Cl_2$: C, 35.79; H, 2.93; N, 5.56. Found: C, 36.11; H, 3.09; N, 5.65. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2164 w, ν_{CO} 1975 vs, 1904 s. IR (KBr, cm^{-1}): ν_{CN} 2179, 2164, ν_{CO} 1965, 1899. ^{1}H NMR (CD_2Cl_2): δ 7.77 [s, 8H$_o$ of BAr'$_4$], 7.60 [s, 4H$_p$ of BAr'$_4$], 4.39 [s, 6H, CH_2SCN], 3.28 [s, 2H, H_{syn}], 2.49 [s, 9H, CH_3 of Ms], 2.06 [s, 3H, CH_3 of methallyl], 1.39 [s, 2H, H_{anti}]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 220.3 [s, CO], 163.3 [c (J(C,B) = 49.8 Hz), C_i of BAr'$_4$], 141.7 [s, $C_{Ms}CH_2$], 136.4 [s, C_o of BAr'$_4$], 131.5 [s, $CMsCH_3$], 130.5 [q (J(C,F) = 31.1 Hz), C_m of BAr'$_4$], 126.2 [c (J(C,F) = 272.5 Hz), CF_3 of BAr'$_4$], 119.1 [s, C_p of BAr'$_4$], 90.1 [s, C_c of methallyl], 61.8 [s, C_t of methallyl], 35.2 [s, CH_2SCN], 21.4 [CH_3 of Ms], 18.1 [s, CH_3 of methallyl].

[Mn(CO)$_3$(Ms(CH$_2$SCN)$_3$)][BAr'$_4$] (3). $[MnBr(CO)_5]$ (0.053 g, 0.182 mmol) was refluxed in MeCN (10 mL) until the disappearance of the ν_{CO} bands of the starting material and the appearance of the ν_{CO} bands of $[MnBr(CO)_3(NCMe)_2]$ (2042 vs, 1955s, and 1934s; ca. 30 min). After in vacuo evaporation to dryness, AgOTf (0.050 g, 0.194 mmol), MeCN (1 mL), and CH_2Cl_2 (10 mL) were added, and the mixture was stirred for 1 h in the dark and filtered through diatomaceous earth. To this solution were added $Ms(CH_2SCN)_3$ (0.045 g, 0.182 mmol) and $NaBAr'_4$ (0.170 g, 0.182 mmol), and after stirring for 1 h, the mixture was filtered through diatomaceous earth. In vacuo concentration and the addition of hexane (10 mL) causes the precipitation of a yellow microcrystalline solid. Crystals of good quality for X-ray analysis were obtained by the slow diffusion of hexane (10 mL) into a concentrated solution of **3** in CH_2Cl_2 at −20 °C. Yield: 0.223 g, 91%. Anal. Calcd for $C_{50}H_{27}BF_{24}MnN_3O_3S_3$: C, 44.96; H, 2.04; N, 3.15. Found: C, 45.03; H, 2.13; N, 3.21. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2196 w, ν_{CO} 2066 s, 1985 s. ^{1}H NMR (CD_2Cl_2): δ 7.72 [s, 8H_o of BAr'$_4$], 7.57 [s, 4H_p of BAr'$_4$], 4.40 [s, 6H, CH_2SCN], 2.49 [s, 9H, CH_3 of Ms]. $^{13}C\{^1H\}$ NMR(CD_2Cl_2): δ 215.1 [s, CO], 161.7 [c (J(C,B) = 50.2 Hz), C_i of BAr'$_4$], 140.34 [s, $C_{Ms}CH_2$], 137.7 [s, C_o of BAr'$_4$], 129.9 [s, $CMsCH_3$], 128.7 [q (J(C,F) = 27.2 Hz), C_m of BAr'$_4$], 124.6 [c (J(C,F) = 272.7 Hz), CF_3 of BAr'$_4$], 120.3 [s, C_p of BAr'$_4$], 117.6 [s, SCN], 33.5 [s, CH_2SCN], 16.8 [CH_3 of Ms].

[Re(CO)$_3$(Ms(CH$_2$SCN)$_3$)][BAr'$_4$] (4). AgOTf (0.035 g, 0.130 mmol) was added to a solution of $[ReBr(CO)_3(NCMe)_2]$ (0.053 g, 0.123 mmol) in a mixture of CH_2Cl_2/MeCN (10 mL/0.5 mL). After stirring for 1 h and filtration through diatomaceous earth, $Ms(CH_2SCN)_3$ (0.043 g, 0.130 mmol) and $NaBAr'_4$ (0.115 g, 0.130 mmol) were added and stirred for 1 h. The mixture was filtered through diatomaceous earth, and in vacuo concentration and the addition of hexane (10 mL) caused the precipitation of a white microcrystalline solid, which was washed with hexane (3 × 10 mL) and dried under vacuum. Yield: 0.166 g, 92%. Anal. Calcd for $C_{50}H_{27}BF_{24}N_3O_3ReS_3$: C, 40.94; H, 1.86; N, 2.86. Found: C, 41.07; H, 1.94; N, 2.95. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2193 w, ν_{CO} 2055 s, 1965 s. IR (KBr, cm^{-1}): ν_{CN} 2196, ν_{CO} 2058, 1971, 1953. ^{1}H NMR (CD_2Cl_2): δ 7.73 [s, 8H_o of BAr'$_4$], 7.58 [s, 4H_p of BAr'$_4$], 4.56 [s, 6H, CH_2SCN], 2.49 [s, 9H, CH_3 of Ms]. $^{13}C\{^1H\}$ NMR(CD_2Cl_2): δ 197.2 [s, CO], 161.7 [c (J(C,B) = 50.2 Hz), C_i of BAr'$_4$], 140.34 [s, $C_{Ms}CH_2$], 137.7 [s, C_o of BAr'$_4$], 129.9 [s, $CMsCH_3$], 128.7 [q (J(C,F) = 27.2 Hz), C_m of BAr'$_4$], 124.6 [c (J(C,F) = 272.7 Hz), CF_3 of BAr'$_4$], 120.3 [s, C_p of BAr'$_4$], 117.6 [s, SCN], 33.5 [s, CH_2SCN], 16.8 [CH_3 of Ms].

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Reaction of 1 with I_2. A solution of I_2 (0.113 g, 0.440 mmol) in CH_2Cl_2 (10 mL) was added, via canula, to a solution of **1** (0.230 g, 0.440 mmol) in CH_2Cl_2 (10 mL) at 0 °C, and the mixture was allowed to reach room temperature and stirred for 15 min. After filtration through diatomaceous earth and in vacuo concentration, the addition of hexane (10 mL) caused the precipitation of a light-brown microcrystalline solid, a mixture of $[MoI_2(CO)_3(Ms(CH_2SCN)_3)]$ (**5**) and $[MoI_2(CO)_3\{Ms(CH_2SCN)_2(CH_2I)\}]$ (**6**). Compound **6** was extracted with CH_2Cl_2 (5 × 5 mL), and by the slow diffusion of hexane into that solution at room temperature, orange crystals of good quality for X-ray analysis were obtained (yield: 0.100 g, 27%). The brown solid sparingly soluble in CH_2Cl_2 corresponded to **5** (yield: 0.070 g, 20%). IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2181w, 2155 w, ν_{CO} 2033vs, 1965s, 1943 sh. Spectroscopic data of **5**. ^1H NMR (acetone-d_6): δ 4.62 (s, 6H, CH_2), 2.32 (s, 9H, CH_3). Insufficient solubility of **5** in all common organic solvents precluded the ^{13}C NMR acquisition. Spectroscopic data of **6**. ^1H NMR (CD_2Cl_2): δ 4.69 (d(12), 2H, CH_2), 4.53 (s, 2H, CH_2), 4.21 (d(12), 2H, CH_2), 2.53 (s, 3H, CH_3), 2.46 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 225.7 [s, CO], 138.9, 137.5, 129.0, 124.0 [s, C_{Ms}], 34.1 [s, CH_2SCN], 16.2, 15.4 [CH_3 of Ms].

$[MoI(CO)_3(Ms(CH_2SCN)_3)][BAr'_4]$ (7). $NaBAr'_4$ (0.195 g, 0.220 mmol) was added to a suspension of **5** (0.170 g, 0.220 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for 1 h. After filtration through diatomaceous earth and in vacuo concentration, the addition of hexane caused the precipitation of **7** as a light-brown microcrystalline solid. Yield: 0.285 g, 86%. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2183 m, ν_{CO} 2062 s, 2006 s, 1984 s. ^1H NMR (CD_2Cl_2): δ 7.87 [s, 8H_o of BAr'_4], 7.69 [s, 4H_p of BAr'_4], 4.48 [s, 6H, CH_2SCN], 2.54 [s, 9H, CH_3 of Ms]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 225.6 [s, CO], 161.9 [c (J(C,B) = 50.2 Hz), C_i of BAr'_4], 140.6 [s, $C_{Ms}CH_2$], 134.9 [s, C_o of BAr'_4], 129.9 [s, $CMsCH_3$], 128.7 [q (J(C,F) = 27.2 Hz), C_m of BAr'_4], 127.0 [s, SCN], 124.6 [c (J(C,F) = 272.7 Hz), CF_3 of BAr'_4], 117.6 [s, C_p of BAr'_4], 33.9 [s, CH_2SCN], 16.5 [CH_3 of Ms].

$[Cu(Ms(CH_2SCN)_3)]_2[BAr'_4]_2$ (8). $[Cu(OTf)]_2\cdot C_6H_6$ (0.050 g, 0.099 mmol) and $Ms(CH_2SCN)_3$ (0.066 g, 0.198 mmol) were stirred in a mixture of THF/MeCN (10 mL/1 mL) until formation of a white precipitate (in a few minutes). After decantation of the solution, the microcrystalline solid was washed with hexane (2 × 10 mL) and redissolved in CH_2Cl_2 (20 mL). $NaBAr'_4$ (0.175 g, 0.198 mmol) was added, and the mixture was stirred for 30 min and filtered through diatomaceous earth. After in vacuo concentration (to ca. 10 mL), the solution was layered with hexane (20 mL) and placed at −20 °C, affording white crystals, one of which was used for determination of the structure of **8** by X-ray diffraction. Yield: 0.427 g, 85%. Anal. Calcd for $C_{47}H_{27}BCuF_{24}N_3S_3$: C, 44.79; H, 2.16; N, 3.33. Found: C, 44.83; H, 2.23; N, 3.38. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2174. IR (KBr, cm^{-1}): ν_{CN} 2189, 2144. ^1H NMR (CD_2Cl_2): δ 7.75 [s, 8H_o of BAr'_4], 7.50 [s, 4H_p of BAr'_4], 4.37 [s, 6H, CH_2SCN], 2.48 [s, 9H, CH_3 of Ms]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.7 [c (J(C,B) = 50.1 Hz), C_i of BAr'_4], 139.3 [s, $C_{Ms}CH_2$], 134.8 [s, C_o of BAr'_4], 131.6 [s, $CMsCH_3$], 129.3 [q (J(C,F) = 33.6 Hz), C_m of BAr'_4], 124.8 [c (J(C,F) = 271.3 Hz), CF_3 of BAr'_4], 118.5 [s, C_p of BAr'_4], 113.2 [s, SCN], 33.9 [s, CH_2SCN], 17.4 [CH_3 of Ms].

$[Ag(Ms(CH_2SCN)_3)]_2[BAr'_4]_2$ (9). A mixture of AgOTf (0.050 g, 0.195 mmol), $Ms(CH_2SCN)_3$ (0.065 g, 0.195 mmol), and $NaBAr'_4$ (0.172 g, 0.195 mmol) in CH_2Cl_2 (10 mL) was stirred in the dark for 1 h. After filtration through diatomaceous earth and in vacuo concentration, the addition of hexane (10 mL) caused the precipitation of a white microcrystalline solid, which was washed and dried under vacuum. By the slow diffusion of hexane (10 mL) into a concentrated solution of **9** in CH_2Cl_2 at −20 °C, white crystals were obtained, one of which was used for the X-ray structure determination. Yield: 0.478 g, 93%. Anal. Calcd for $C_{47}H_{27}AgBF_{24}N_3S_3$: C, 43.27; H, 2.09; N, 3.22. Found: C, 43.33; H, 2.14; N, 3.27. IR (CH_2Cl_2, cm^{-1}): ν_{CN} 2168. ^1H NMR (CD_2Cl_2): δ 7.76 [s, 8H_o of BAr'_4], 7.60 [s, 4H_p of BAr'_4], 4.34 [s, 6H, CH_2SCN], 2.52 [s, 9H, CH_3 of Ms]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.8 [c (J(C,B) = 49.8 Hz), C_i of BAr'_4], 139.4 [s, $C_{Ms}CH_2$], 134.9 [s, C_o of BAr'_4], 130.3 [s, $CMsCH_3$], 129.1 [q (J(C,F) = 31.6 Hz), C_m of BAr'_4], 124.7 [c (J(C,F) = 272.3 Hz), CF_3 of BAr'_4], 117.6 [s, C_p of BAr'_4], 114.3 [s, SCN], 32.5 [s, CH_2SCN], 16.8 [CH_3 of Ms].

Cyclopropanation. A solution of EDA (1 mmol, 0.105 mL) in CH_2Cl_2 (10 mL) was added, over the time indicated, using a syringe pump and a Hamilton gastight 20 mL syringe to a solution of **8** (0.005 mmol, 12.6 mg) and the olefin (5 mmol) dissolved in CH_2Cl_2 (15 mL). The solution was stirred for 2 h after the complete addition of EDA. An internal standard, C_6Me_6 (0.055 mmol, 9 mg), was added. An aliquot (1 mL) was then filtered through a plug of silica gel, and the solution was concentrated to ~0.5 mL. $CDCl_3$ (0.5 mL) was added, and the sample was transferred to an NMR tube. Yields were estimated using ^1H NMR spectroscopy by integration of product resonances relative to the internal hexamethylbenzene standard. Only for cyclopropane from styrene did the signals due to the different diasteromers appear at sufficiently different chemical shifts so that their integration could be used to obtain an estimation of the trans/cis ratio.

Aziridination. To a mixture of **8** (0.01 mmol, 24 mg), the olefin (5 mmol), and 4 Å molecular sieves (ca. 1 g) in 15 mL of CH_2Cl_2 was added PhI=NTs (1 mmol, 348 mg), and the mixture was stirred until PhI=NTs was completely dissolved (5 h). An internal standard, C_6Me_6 (0.055 mmol, 9 mg), was added. An aliquot (1 mL) was filtered through silica gel and concentrated to ~0.5 mL. $CDCl_3$ (0.5 mL) was added, and the sample was transferred to an NMR tube. Yields were estimated using ^1H NMR spectroscopy by integration of product resonances relative to the internal standard.

Cyclopropenation. A solution of EDA (1 mmol, 0.105 mL) in CH_2Cl_2 (10 mL) was added over 11 h using a syringe pump to a solution containing **8** (0.005 mmol, 12.6 mg) and the alkyne (5 mmol) in CH_2Cl_2 (15 mL). The solution was stirred for 2 h after the complete addition of EDA. Analysis of the results was as described for cyclopropanation.

X-ray Crystallography. Crystallographic data for $Ms(CH_2SCN)_3$, **1**, **2**, **8**, and **9** were collected with a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) for **1**, **2**, and **9** and Cu Kα radiation (λ = 1.5418 Å) for **8** and a CCD area detector. Raw frame data were integrated with the program *SAINT*.[42] A semiempirical absorption correction was applied with the program *SADABS*.[43] Trifluoromethyl groups are disordered in **8**. For compound **6**, data collection was performed on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu Kα (λ = 1.5418 Å). The intensities were measured using the oscillation method. The crystal structure was solved by direct methods. The refinement was performed using full-matrix least squares on F^2. Crystal structures were solved by direct methods, using the program *SIR-92*[44] under *WINGX*[45] and refined against F^2 with *SHELXTL-97*.[46] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to $1.2U_{eq}$ of the atoms to which they are attached (1.5 for methyl groups). Flack parameter:[47] 0.08(1).

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Table 5

	$Ms(CH_2SCN)_3$	**1**	**2**
empirical formula	$C_{15}H_{15}N_3S_3$	$C_{19}H_{17}Cl_2MoN_3O_3S_3$	$C_{54}H_{36}BCl_2F_{24}MoN_3O_3S_3$
fw	333.48	598.35	1488.69
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
a (Å)	8.808(9)	10.317(2)	10.496(11)
b (Å)	10.401(11)	15.328(3)	17.091(18)
c (Å)	10.617(11)	15.115(3)	18.91(2)
α (deg)	63.225(19)	90	72.58(2)
β (deg)	73.88(2)	102.84(3)	74.470(19)
γ (deg)	76.59(2)	90	72.62(2)
V (Å^3)	827.8(15)	2330.6(8)	3029(5)
Z	2	4	2
T (K)	293(2)	293(2)	293(2)
D_{calc} (g cm^{-3})	1.338	1.665	1.632
F(000)	348	1168	1484
λ(Kα) (Å)	0.710 73	1.5418	0.710 73
cryst size (mm)	0.27 × 0.14 × 0.06	0.25 × 0.12 × 0.10	0.48 × 0.47 × 0.21
μ(Kα) (mm^{-1})	0.444	9.448	0.526
collection range (deg)	2.19−23.78	4.16−68.75	1.15−23.36
max/min transm factors	1.000/0.576	1.201/0.841	1.000/0.703
reflns collected	3784	17 758	13 480
indep reflns [R(int)]	2405 [0.0281]	4192 [0.0426]	8526 [0.0191]
GOF on F^2	0.978	1.117	1.028
R1, wR2 (all data)	0.0754, 0.1389	0.0469, 0.1203	0.0815, 0.1888
R1, wR2 [$I > 2\sigma(I)$]	0.0513, 0.1271	0.0415, 0.1021	0.0687, 0.1744
largest diff peak	0.329, −0.289	0.843, −0.688	1.207, −0.702

	3	**6**	**8**	**9**
empirical formula	$C_{168}H_{96}B_3F_{72}Mn_4N_{12}O_{12}S_3$	$C_{17}H_{15}I_3MoN_2O_3S_2$	$C_{47}H_{27}BCuF_{24}N_3S_3$	$C_{94}H_{54}Ag_2B_2F_{48}N_6S_6$
fw	1335.67	836.09	1260.25	2609.15
cryst syst	cubic	orthorhombic	triclinic	triclinic
space group	$P\bar{4}3n$	$Pbca$	$P\bar{1}$	$P\bar{1}$
a (Å)	21.6980(1)	17.6096(4)	13.1045(2)	13.154(3)
b (Å)	21.6980(1)	9.7609(2)	13.1857(2)	13.204(3)
c (Å)	21.6980(1)	27.6001(5)	16.1827(2)	16.343(3)
α (deg)	90	90	80.3460(9)	83.39(3)
β (deg)	90	90	84.7997(10)	78.76(3)
γ (deg)	90	90	64.6597(11)	64.24(3)
V (Å^3)	10215.49(8)	4744.06(17)	2490.85(7)	2506.0(9)
Z	2	8	2	2
T (K)	150(2)	293(2)	150(2)	150(2)
D_{calc}(g cm^{-3})	1.456	2.341	1.680	1.729
F(000)	4478	3104	1256	1292
λ(Kα) (Å)	1.5418	1.5418	1.5418	1.5418
cryst size (mm)	0.37 × 0.25 × 0.25	0.043 × 0.086 × 0.203	0.22 × 0.20 × 0.01	0.22 × 0.20 × 0.05
μ(Kα) (mm^{-1})	4.208	37.004	2.982	0.656
collection range (deg)	2.88−68.21	3.20−74.00	2.77−68.31	1.27−68.90
max/min transm factors	1.47/0.82	1.00/0.18	0.97/0.86	0.84/1.15
reflns collected	5881	19 275	39 612	38 201
indep reflns [R(int)]	3129 [0.0253]	4787 [0.0743]	9011 [0.0360]	9115 [0.0411]
GOF on F^2	1.041	1.059	1.090	1.031
R1, wR2 (all data)	0.0837, 0.2272	0.0648, 0.1699	0.0754, 0.1861	0.0788, 0.1940
R1, wR2 [$I > 2\sigma(I)$]	0.0777, 0.2187	0.0609, 0.1651	0.0684, 0.1781	0.0718, 0.1856
largest diff peak	0.616, −1.295	2.010, −2.247	1.205, −1.088	1.659, −1.077

For compound **3**, data collection was performed at 150(2) K on a Nonius Kappa CCD single-crystal diffractometer, using Cu Kα radiation ($\lambda = 1.5418$ Å). Images were collected at a 29 mm fixed crystal−detector distance, using the oscillation method, with 2° oscillation and 30 s exposure time per image. The data collection strategy was calculated with the program *Collect*.[48] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[49] Unit cell dimensions were determined from 18 112 reflections between $\theta = 2.2°$ and 68.2°. Multiple observations were averaged, $R_{merge} = 0.0253$, resulting in 3129 unique reflections, of which 2759 were observed with $I > 2\sigma(I)$. A semiempirical absorption correction was applied using the program *SORTAV*.[50] Trifluoromethyl groups are disordered. The crystal structure exhibits some voids that may be filled with crystallization solvents (hexane and dichoromethane). However, these solvents could not be appropiately modeled, and the residual density in these spaces was removed using the *SQUEEZE* procedure,[51] as implemented in the program *PLATON*.[52] The final cycle of full-matrix least-squares refinement based on 3129 reflections and 251 parameters converged to a final value of R1[$F^2 > 2\sigma(F^2)$] = 0.0777, wR2[$F^2 > 2\sigma(F^2)$] = 0.2187, R1(F^2) = 0.0837, wR2(F^2) = 0.2272. Final difference Fourier maps showed no peaks higher than 0.616 e Å^{-3} or deeper than −1.295 e Å^{-3}.

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For compounds **2**, **3**, **8**, and **9**, containing the anion BAr'_4, the trifluoromethyl groups are affected by some degree of disorder. Only in some cases for structures **3** and **8** was it possible to find a correct model for alternate (staggered) positions. In the remaining cases, the incipient disorder affects the shape and size of the ellipsoids of the fluorine atoms, which are abnormally bigger when compared to those of the pivotal carbon atoms in which they ride (Table 5).

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Supporting Information Available: X-ray crystallographic data in CIF format, molecular representation of the crystal structures of **3** and **8**, VT ^1H NMR of **5** in CD_2Cl_2, ^{13}C NMR of **7** at room temperature and −60 °C, and references giving the spectroscopic data of the catalysis products. This material is available free of charge via the Internet at http://pubs.acs.org.