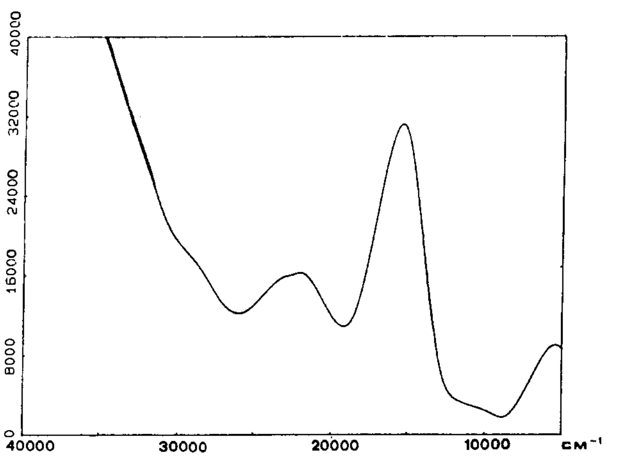

**Figure 2.** Electronic spectrum of $[Ru_2(bpy)_4(tetrox)](PF_6)_3$ in acetonitrile solution.

lowest so far reported for mixed-valence ruthenium complexes and the extinction coefficient (9300 $M^{-1}$ $cm^{-1}$) is the highest. High intensity of the transition and low frequency are characteristic of class III mixed-valence compounds. An additional feature of the spectra of these compounds is the relative insensitivity of the frequency maxima to changes in solvent. The spectral region in which we observe the maximum absorption for the intervalence band of **3** is very difficult to investigate, due to the presence of absorption bands of the solvents and to low sensitivity of the spectrophotometers, which prevent accurate analysis. However, we observe that the absorption maximum does not shift more than 100 $cm^{-1}$ in DMF, acetone, and DMSO, thus providing additional evidence of class III behavior. Furthermore, the experimental half-height bandwidth ($\Delta\nu_{1/2}$) is ca. 3000 $cm^{-1}$, lower than expected from the theory for a pure class II mixed-valence system. In fact, a value of 3330 $cm^{-1}$ is calculated with the use of the Hush formula[13]

$$\Delta\nu_{1/2} = (2310E_{op})^{1/2}\ cm^{-1}$$

where $E_{op}$ is the absorption maximum of the intervalence transition. The class III behavior of **3** must be associated with the extent of the electron delocalization toward the bridging ligands evidenced by the EPR spectra.

$[Ru_2(bpy)_4(tetrox)](PF_6)_4$ (**4**) is diamagnetic. Possible descriptions are either $[Ru^{III}_2(bpy)_4(tetrox^{2-})]^{4+}$ or $[Ru^{II}_2(bpy)_4(tetrox)]^{4+}$. One-electron oxidation of a $Ru^{III}$–$Ru^{II}$ moiety usually yields a dinuclear ruthenium(III) derivative. Under this hypothesis the observed magnetic properties of this compound might be explained, assuming that a strong antiferromagnetic interaction between the two metal ions is operative. Although this possibility cannot be discarded, previous studies on 3d dinuclear complexes of this ligand led us to consider this hypothesis as highly unprobable.[23,26] Therefore we conclude that **4** must be described as containing two ruthenium(II) ions bridged by uncharged 1,4,5,8-naphthodiquinone. Indeed one-electron oxidation of the $[Ru_2(bpy)_4(tetrox)]^{3+}$ cation involves the reduction of the ruthenium(III) ion and the two-electron oxidation of the ligand. A similar behavior has been suggested to occur for oxidation processes involving some $Ru^{III}$–catecholate adducts, which yield products to be described as $Ru^{II}$–quinone derivatives.[24] A confirmation of this assignment comes from the electronic spectrum of **4**, which is different from those of both **2** and **3**, with a maximum at 17 300 $cm^{-1}$, which can be compared to the absorption at 19 500 $cm^{-1}$ for the uncharged tetrox ligand. In this case the observed decrease in the transition energy might be consistent with π interactions involving metal and ligand orbitals.

Since the metal and ligand orbitals are of comparable energies, we conclude therefore, in agreement with Lever et al.,[18] that the nature of the frontier orbitals for the $[Ru_2(bpy)_4tetrox]^{n+}$ cations depends on the relative stabilization of the ruthenium and tetrox orbitals upon oxidation. In **2** the metal orbitals are higher in energy than the ligand orbitals. Upon one-electron oxidation, the metal orbitals are more stabilized than the tetrox orbitals and, even if the SOMO of **3** is essentially a metal orbital, a contribution from the ligand orbital must not be neglected. Further, one-electron oxidation stabilizes the metal orbitals more, to such an extent that in **4** the orbital order is reversed and the frontier orbitals have more tetrox character. Therefore **4** is a ruthenium(II)–tetrox complex.

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# Adducts of π-Acceptor Ligands with Copper(I) Thiolates

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A number of recent publications from this laboratory have described the direct electrochemical synthesis of copper(I) thiolates and their adducts,[1-3] and as in related cases, the advantages of the method include simplicity and high product yield. The richness and variety of the range of molecular structures which have been identified for these copper(I) compounds is indeed remarkable,[4-6] and a recent report suggests that similar results may be expected for analogous diorganophosphido derivatives.[7] We have now extended the electrochemical studies to the synthesis of a range of copper(I)–thiolato compounds with the monodentate ligands triphenylphosphine and *tert*-butyl isocyanide, and with phenyl isothiocyanate. A number of the products were also obtained by direct reaction between the copper(I) thiolate and ligand in nonaqueous solution. As in earlier work on these systems, we find that the stoichiometry of the product depends upon the nature of the organic group attached to sulfur.

## Experimental Section

**General Data.** Solvents were distilled from calcium hydride and stored over molecular sieves.

Copper anodes were foils, 0.25 mm thick with a total surface area of ca. 5 $cm^2$. The metal was treated successively with concentrated nitric acid and distilled water, dried, abraded lightly with fine sandpaper, and finally polished with tissue paper.

Thiols, triphenylphosphine, phenyl isothiocyanate (Aldrich), and *tert*-butyl isocyanide (Fluka) were used as supplied.

Copper analysis was by atomic absorption spectrophotometry, using an IL 251 instrument. Microanalysis was carried out by Guelph Chemical Laboratories Ltd. Infrared spectra were obtained with a Nicolet 5DX interferometer, and NMR spectra were recorded on Varian EM 360, Bruker 300 ($^1H$), and Bruker 200 ($^{31}P$) spectrometers. Mass spectra were run on a Varian MAT CH-5 instrument operating in the electron impact mode.

**Electrochemical Procedures.** The electrochemical syntheses followed the methods used previously,[1-3] with cells of the general form

$$Pt(-)/CH_3CN + RSH + L/Cu(+)$$

$$L = P(C_6H_5)_3,\ C_6H_5NCS,\ t\text{-}C_4H_9NC$$

Details of solution composition, length of experiment, etc. are given in

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**Table I.** Experimental Conditions for the Electrochemical Synthesis of Adducts of Copper(I) Thiolates

| | soln compn[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| thiol | amt of RSH, mL | ligand | mass, g | applied[b] voltage, V | time of electrolysis, h | amt of metal consumed, mg | $E_F$[c] | product |
| $CH_3CH_2C(CH_3)_2SH$ | 2 | $Ph_3P$ | 4.9 | 10 | 4.2 | 504 | 1.02 | $CuSC_5H_{11}\cdot 0.5PPh_3$ |
| $C_6H_5SH$ | 2 | $Ph_3P$ | 5.4 | 15 | 2 | 238 | 1.01 | $CuSC_6H_5\cdot 0.5PPh_3$ |
| *o*-$CH_3C_6H_4SH$ | 2 | $Ph_3P$ | 5.1 | 15 | 3 | 356 | 1.00 | $CuSC_6H_4CH_3\cdot 2PPh_3$ |
| *m*-$CH_3C_6H_4SH$ | 2 | $Ph_3P$ | 5.1 | 20 | 2 | 252 | 1.06 | $CuSC_6H_4CH_3\cdot 2PPh_3$ |
| *p*-$CH_3C_6H_4SH$ | 2 | $Ph_3P$ | 5.1 | 20 | 4 | 482 | 1.02 | $CuSC_6H_4CH_3\cdot 1.5PPh_3$ |
| 2-$C_{10}H_7SH$ | 1.1 (g) | $Ph_3P$ | 5.0 | 25 | 2 | 240 | 1.01 | $CuSC_{10}H_7\cdot 1.5PPh_3$ |
| $CH_3CH_2C(CH_3)_2SH$ | 2 | PhNCS | 4 (mL) | 20 | 4 | 480 | 1.02 | $CuSC_5H_{11}\cdot 0.5PhNCS$ |
| *o*-$CH_3C_6H_4SH$ | 1 | *t*-BuNC | 1 (mL) | 20 | 2 | 240 | 1.01 | $CuSC_5H_{11}\cdot$*t*-BuNC |

[a] Dissolved in 50 mL of $CH_3CN$ containing ca. 50 mg of tetraethylammonium perchlorate. [b] Voltage required to produce an initial current of 50 mA. [c] Defined as moles of Cu consumed per faraday of charge.

**Table II.** Analytical Results for Adducts of Copper(I) Thiolates

| | % found | | | | % calcd | | | |
|---|---|---|---|---|---|---|---|---|
| compd | Cu | C | H | N | Cu | C | H | N |
| $CuSC_5H_{11}\cdot 0.5PPh_3$[a] | 20.9 | | | | 21.4 | | | |
| $CuSC_5H_{11}\cdot 0.5PPh_3$[b] | 20.9 | | | | 21.4 | | | |
| $CuSC_6H_5\cdot 2PPh_3$ | 8.51 | 72.5 | 5.31 | | 9.12 | 72.4 | 5.02 | |
| $CuSC_6H_4CH_3$-*o*·$2PPh_3$ | 8.31 | 73.0 | 5.42 | | 8.93 | 72.6 | 5.24 | |
| $CuSC_6H_4CH_3$-*m*·$2PPh_3$ | 8.50 | | | | 8.93 | | | |
| $CuSC_6H_4CH_3$-*p*·$1.5PPh_3$ | 9.85 | | | | 11.0 | | | |
| $CuSC_{10}H_7\cdot 1.5PPh_3$ | 9.81 | 72.7 | 5.15 | | 10.3 | 72.1 | 4.83 | |
| $CuSC_5H_{11}\cdot 0.5PhNCS$ | 26.9 | 43.4 | 5.94 | 3.05 | 27.2 | 43.6 | 5.77 | 2.99 |
| $CuSC_5H_{11}\cdot 0.5PhNCS$[b] | 26.5 | 43.6 | 6.23 | 2.75 | 27.2 | 43.6 | 5.77 | 2.99 |
| $CuSC_6H_4CH_3$-*o*·*t*-BuNC | 22.9 | | | | 23.6 | | | |
| $CuSC_5H_{11}\cdot$*t*-BuNC | 25.0 | 49.0 | 8.51 | 6.51 | 25.5 | 48.1 | 8.01 | 5.61 |
| $CuSC_6F_4H\cdot$tmen[c] | 17.1 | | | | 17.6 | | | |

[a] $-SC_6H_{11}$ = 2-methylbutane-2-thiolate. [b] Products prepared by direct chemical reaction. [c] $-SC_6F_4H$ = 2,3,5,6-tetrafluorobenzenethiolate.

**Table III.** $^1H$ and $^{31}P$ NMR Data for Adducts of Copper(I) Thiolates

| compd | $^1H$[a] | | $^{31}P$[b] |
|---|---|---|---|
| $CuSC_5H_{11}\cdot 0.5PPh_3$ | 7.8–7.2 m (15 H) | 1.79 q (4 H), 1.53 s (12 H), 1.01 t (6 H) | −4.78 |
| $CuSC_6H_5\cdot 2PPh_3$ | 7.4–6.6 m | | −4.74 |
| $CuSC_6H_4CH_3$-*o*·$2PPh_3$ | 7.47–6.91 m (34 H) | 2.41 s (3 H) | −4.27 |
| $CuSC_6H_4CH_3$-*m*·$2PPh_3$ | 7.78–6.58 m (34 H) | 1.82 s (3 H) | −4.25 |
| $CuSC_6H_4CH_3$-*p*·$1.5PPh_3$ | 7.79–6.51 m (53 H) | 2.15 s (6 H) | −4.32 |
| $CuSC_{10}H_7\cdot 1.5PPh_3$ | 7.66–7.11 m | | −3.92 |
| $CuSC_5H_{11}\cdot 0.5PhNCS$ | 7.41–7.08 m | 2.19 q, 1.91 q, 1.71 s, 1.51 s, 1.41 s, 1.40 s, 1.09 t, 0.86 t | |
| $CuSC_5H_{11}\cdot$*t*-BuNC | | 2.53 s (3 H), 1.30 s (9 H) | |
| $CuSC_6H_4CH_3$-*o*·*t*-BuNC | | 1.65 q (2 H), 1.48 s (9 H), 1.29 s (6 H), 0.94 t (3 H) | |

[a] In $CD_2Cl_2$ solution; ppm from $Me_4Si = 0$. [b] In $C_6H_6$ solution; ppm from 85% $H_3PO_4 = 0$; $Ph_3P$ has the $^{31}P$ resonance at −5.48 ppm in this solvent.

Table I. All preparations were carried out with a stream of dry nitrogen bubbling through the solution phase, so that no mechanical stirring was necessary.

As the electrolysis proceeded, hydrogen gas formed at the cathode. The ease with which the product compounds deposited from the solution phase depended on the system in question. In the case of $P(C_6H_5)_3$ and $C_6H_5SH$, *o*-$CH_3C_6H_4SH$, or $C_{10}H_7SH$-2, the solution began to turn yellow as soon as electrolysis occurred, followed shortly by the precipitation of the yellow solid adduct, and precipitation was essentially complete by the end of the electrolysis. For $P(C_6H_5)_3$ and $C_5H_{11}SH$, *m*-$CH_3C_6H_4SH$, or *p*-$CH_3C_6H_4SH$, and for $C_6H_5NCS$ and $C_5H_{11}SH$ ($C_5H_{11} = CH_3CH_2C(CH_3)_2$), precipitation took place more slowly and continued over a period of about 12 h after the current had ceased to flow. In the case of *o*-$CH_3C_6H_4SH$ and *t*-$C_4H_9NC$, traces of a white solid precipitated during the electrolysis; this material was removed by filtration, the filtrate taken to dryness in vacuo, and the residue treated with diethyl ether. Slow evaporation of this extract solution gave colorless crystals of $CuSC_6H_4CH_3$-*o*·*t*-$C_4H_9NC$. The yields of the products obtained by these procedures were 90% or better, based on the quantity of metal dissolved.

The products were characterized by elemental analysis (Table II) and by infrared and NMR ($^1H$, $^{31}P$) spectroscopy (Table III), which established the presence of the appropriate thiolate and neutral ligand. The adducts are soluble in benzene and chlorinated hydrocarbon solvents and are air-stable.

**Two-Step Syntheses.** We also prepared adducts of $CuSC_5H_{11}$ by first synthesizing the copper(I) thiolate by the electrochemical techniques described previously[1] and then treating this material with the neutral ligand. In each case, the product was analytically and spectroscopically identical with that synthesized by the one-step method described above.

**(i) $CuSC_5H_{11}$ + $P(C_6H_5)_3$.** A solution of $P(C_6H_5)_3$ (2.58 g, 9.85 mmol) in acetonitrile (20 mL) was added to $CuSC_5H_{11}$ (0.50 g, 3.0 mmol) and the mixture stirred mechanically at room temperature for 2 days, during which time the yellow color of the solid discharged. The final colorless solid was collected by filtration, washed with cold acetonitrile (10 mL), and dried in vacuo. The yield of $CuSC_5H_{11}\cdot 0.5P(C_6H_5)_3$ was almost quantitative, based on $CuSC_5H_{11}$.

**(ii) $CuSC_5H_{11}$ + *t*-$C_5H_9NC$.** When *tert*-butyl isocyanide (0.8 mL, 0.65 g, 7.65 mmol) was added to a suspension of $CuSC_5H_{11}$ (0.50 g, 3.0 mmol) in acetonitrile (30 mL), the suspended yellow solid immediately dissolved to give a colorless solution, whose volume was reduced in vacuo to ca. 10 mL. Colorless crystals deposited over a 12-h period at room temperature and were collected, washed with cold acetonitrile (10 mL), and dried in vacuo; yield of $CuSC_5H_{11}\cdot$*t*-$C_4H_9NC$ 80%.

**(iii) $CuSC_5H_{11}$ + $C_6H_5NCS$.** Phenyl isothiocyanate (2 mL, 3.3 g, 24.4 mmol) was added to a suspension of $CuSC_5H_{11}$ (0.50 g) in acetonitrile (60 mL), and the mixture was heated to 50 °C, at which point the solid dissolved. The yellow solid that deposited when this solution was cooled to room temperature was collected, washed (cold $CH_3CN$, 15 mL), and dried in vacuo; yield of $CuSC_5H_{11}\cdot 0.5C_6H_5NCS$ 90%. The mass spectrum of this compound had prominent ions at the following *m/e* values: 666, $[CuSC_5H_{11}]_4^+$; 595, $[Cu_4(SC_5H_{11})_3S]^+$; 524, $[Cu_4(SC_5H_{11})_2S_2]^+$; 453, $[Cu_4(SC_5H_{11})S_3]^+$; 382, $[Cu_4S_4]^+$; 238, $[C_6H_5NCSSC_5H_{11}]^+$; 206, $[C_6H_5NCSC_5H_{11}]^+$; 135, $[C_6H_5NCS]^+$; 103, $[C_5H_{11}S]^+$; 77, $[C_6H_5]^+$.

**Attempted Reaction with Carbon Monoxide: $CuSC_6F_4H$-2,3,5,6 + CO.** No interaction was observed when carbon monoxide gas (1 atm pressure) was bubbled through an electrolytic cell of the type described above. In a subsequent experiment, $CuSC_6F_4H$ (0.10 g, 0.41 mmol) was suspended in $CH_2Cl_2$ (30 mL) and a stream of CO flowed through the mixture, at atmospheric pressure, for 30 min. No sign of reaction was detected, either visibly or by monitoring the infrared spectrum in the $\nu(C{\equiv}O)$ region. When *N,N,N',N'*-tetramethylethanediamine (tmen; 0.2 mL, 0.28 g, 2.5 mmol) was added, the yellow solid dissolved to give a colorless solution, whose infrared spectrum had a strong band at 2074 $cm^{-1}$. All attempts to isolate a solid containing carbon monoxide were unsuccessful, and evaporation of the colorless solution in vacuo gave $CuSC_6F_4H{\cdot}tmen$.

## Results

**Electrochemistry and Preparation.** The adducts of copper(I) thiolates with triphenylphosphine, phenyl thiocyanate, and *tert*-butyl isocyanide are easily prepared in good yield by the simple one-step method described, in keeping with previous work on related systems.[1,2] Although the stoichiometry of the $CuSR{\cdot}nL$ products clearly depends on both R and L (see below), the electrochemical efficiency, defined as the quantity of copper dissolved per faraday of charge, is 1.02 ± 0.02 mol/faraday for the whole range of electrochemical syntheses reported in Table I. This result is in keeping with the mechanism proposed in earlier papers.[1,2] The constancy of the $E_F$ values in Table I shows that the stoichiometry of the adducts is independent of the initial mode of formation of CuSR.

$$\text{cathode:}\quad RSH + e^- \rightarrow \tfrac{1}{2}H_2(g) + RS^- \tag{1}$$

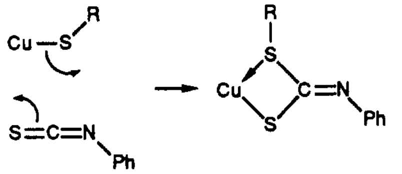
$$\text{anode:}\quad RS^- + Cu \rightarrow CuSR + e^- \tag{2}$$

As noted in the Experimental Section, we also showed that in the case of $CuSC_5H_{11}$, the adducts can also be prepared directly from mixtures of the two components under relatively mild conditions, which provides further confirmation of the importance of processes subsequent to the electrochemical formation of CuSR.

**Spectroscopy.** In addition to confirming the presence of the appropriate thiolato and neutral ligands, the infrared spectra gave useful information as to the mode of bonding. In the case of $t$-$C_4H_9NC$, a strong absorption at 2152 $cm^{-1}$ in $CuSC_5H_{11}{\cdot}t$-$C_4H_9NC$ is matched in intensity and frequency by that at 2161 $cm^{-1}$ in $CuSC_6H_4CH_3$-$o$-$t$-$C_4H_9NC$. Floriani and co-workers[8] have prepared compounds of the type $Cu_2(\mu\text{-}OC_6H_5)_2(RNC)_2$ (R = $C_6H_{11}$, $p$-$CH_3C_6H_4$), which also show absorptions in the 2120–2160-$cm^{-1}$ region, assigned as $\nu(C{\equiv}N)$, and similar modes were found[9] in isocyanide derivatives of dinuclear copper(I) benzoate compounds $Cu_2(\mu\text{-}O_2CC_6H_5)_2(RNC)_2$. While the similarities in these $\nu(C{\equiv}N)$ modes do not establish the overall structure of the thiolate derivatives, they do demonstrate the identity of the $Cu{-}C{\equiv}N{-}$ bonding in all of these compounds, some of which have been studied by X-ray crystallography,[8,9] and the stoichiometry of the $CuS_5H_{11}$ adduct obviously fits with a dimeric structure.

The infrared spectrum of $CuSC_5H_{11}{\cdot}0.5C_6H_5NCS$ has, inter alia, strong absorptions at 1493 and 962 $cm^{-1}$, assigned to $\nu(C{=}N)$ and $\nu(C{=}S)$ of the isocyanate ligand. The former value lies between those of $\nu(C{-}N)$ and $\nu(C{=}N)$, implying some weakening of the C=N bond. The mass spectrum of this compound (Experimental Section), which identifies a number of ions derived from $C_6H_5NCS$ and $C_5H_{11}S$, is also similar to that of $Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4$ (**1**) in the high $m/e$ region.[3] Following the argument presented in the discussion of the latter structure, we conclude that decomposition in the ion source yields $(CuSC_5H_{11})_n$, which then gives rise to these large ions. The $^1H$ NMR spectrum of this compound (Table III) has a number of features in the $C_5H_{11}$ region resembling those of **1**, and the assignments follow those for that compound on the assumption that both compounds involve two types of ligands, $C_5H_{11}S$ and $C_5H_{11}(L)S$ (L = $CS_2$ or $C_6H_5NCS$). The terminal methyl group gives rise to two triplets (0.86 and 1.09 ppm), and the $CH_2$ group generates two quartets (1.91 and 2.19 ppm), while in the $\alpha$-$CH_3$ region there are four resonances, identified as a pair of doublets (1.40 + 1.41 and 1.51 + 1.71 ppm). The resonances at 0.86, 1.91, and 1.40 + 1.41 ppm are believed to arise from the $C_5H_{11}S^-$ ligand, and these values differ from those in **1** by 0.16 ± 0.01 ppm, while the remaining resonances are due to $[C_5H_{11}(C_6NCS)S]^-$ (see below), and the chemical shift differences from those assigned in the spectrum of **1** due to $C_5H_{11}SCS_2^-$ are in the range 0.4–0.2 ppm.

The structure of **1** has been shown to be based on a $Cu_8S_{12}$ cage with both thiolato and thioxanthato ligands, with mono-, bi-, and tridentate modes of coordination. The thioxanthate is generated from the reaction of $CuSC_5H_{11}$ with $CS_2$, by a process that can be formally described as the insertion of $CS_2$ into half of the Cu–S bonds of the parent compound. We believe that the analogy between $CS_2$ and PhNCS, and the similarities in the spectroscopic properties of **1** and $CuSC_5H_{11}{\cdot}0.5C_6H_5NCS$, provide reasonable evidence that the latter can be formulated as $Cu_8(SC_5H_{11})_4[S_2(C_5H_{11})CNC_6H_5]_4$. The insertion of PhNCS is then assumed to proceed via a mechanism which is in essence



(3)

Further studies of such systems are planned.

The most interesting spectral feature of the various triphenylphosphine adducts lies in the $^{31}P$ NMR results. In each case, there is a small upfield shift from the resonance of the free ligand, which is consistent with published results for monodentate $P(C_6H_5)_3$ in a variety of copper(I) derivatives.[10-12] Unfortunately, these values offer no diagnostic aid in establishing possible structures for the CuSR adducts, for which the number of coordinated $P(C_6H_5)_3$ molecules varies from 0.5 to 2 per copper atom. Given the variety of structures that have been reported for neutral and anionic copper(I) thiolate complexes,[1,3,5,6] it seems pointless to speculate on the structures of these compounds. The ratio of 1.5 $P(C_6H_5)_3$ per copper atom in the $C_{10}H_7S$ and $p$-$CH_3C_6H_4S$ derivatives represents an unusual stoichiometry, which does not appear to have been reported previously. In general, the solubility of the triphenylphosphine–CuSR adducts suggests that these compounds have low molecularity.

**The $CuSC_6F_4H$–CO System.** Although it was not possible to obtain a solid copper(I) thiolate derivative containing carbon monoxide, we did find clear evidence of complexing between CO and $CuSC_6F_4H$ in solutions containing tmen. The strong infrared absorption at 2074 $cm^{-1}$ is typical of that found in copper(I) complexes with terminal CO ligands.[13,14]

## Discussion

The methods reported lead to the synthesis of a variety of complexes involving copper(I) thiolates and neutral ligands whose bonding to transition metals in low oxidation states is generally described in terms of L → M $\sigma$-donation and M → L $\pi$-back-donation. The electrochemical synthesis clearly gives rise to the appropriate copper(I) thiolates by anodic oxidation, but the subsequent formation of the adducts appears to involve some slow processes in the solution phase. Any discussion as to the factors that affect the structure and stoichiometry of these, and other, copper(I) thiolate adducts clearly goes beyond the present preparative and spectroscopic evidence.

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