

(terminal CO), 1551 (m), 1510-1410 (several not well-resolved bands of medium intensities).

Crystal Structure Determination of $\text{Re}(\text{CO})_5\text{C}(\equiv\text{O})\text{C}(\equiv\text{O})\text{Re}(\text{CO})_5$. Crystals data: $\text{C}_{12}\text{O}_{12}\text{Re}_2$; $M_r = 708.4$; monoclinic; space group $P2_1/c$ (No. 14); $a = 6.527$ (4) Å, $b = 12.392$ (6) Å, $c = 10.192$ (6) Å, $\beta = 95.69$ (8)°; $U = 820.2$ (7) Å³; $D_{\text{calcd}} = 2.87$ g cm⁻³; $Z = 2$; graphite-monochromated X radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 150.1$ cm⁻¹.

A small crystal (ca. $0.18 \times 0.2 \times 0.3$ mm) was mounted under N_2 in a thin-walled glass capillary for data collection. Data were collected at 220 K on a Nicolet P3m diffractometer, the low temperature being necessary to minimize crystal decomposition in the X-ray beam. A correction was applied for the ca. 20% decay that occurred during the course of the diffraction experiment. A total of 1576 intensity data were collected in the range $4^\circ < 2\theta < 50^\circ$ and corrected for absorption by an empirical method (based on 235 azimuthal scan data, transmission coefficients varied between 0.010 and 0.035). Of these, 1240 were unique observations of which 1168 with $F^2 > 2\sigma(F^2)$ were used in the structure solution and refinement. The structure was determined by conventional heavy-atom methods (Patterson and Fourier) and refined, with all atoms assigned anisotropic vibrational parameters, by blocked-cascade full-matrix least squares to final residual indices $R = 0.038$, $R_w = 0.038$, and $s = 1.32^{23}$ (weights $w = (4\sigma(F_o^2)/F_o^2 +$

$0.0008F_o^2)^{-1}$ with $\sigma(F_o^2)$ based on counting statistics alone). A final difference electron density Fourier synthesis showed no features of magnitude >2.7 e Å⁻³, the largest peaks being less than ca. 1 Å from the metal atoms.

Registry No. $[\text{Mn}_2(\text{CO})_{10}]\text{C}(\text{O})\text{C}(\text{O})$, 92641-65-1; $[\text{Re}_2(\text{C}(\text{O})_{10})\text{C}(\text{O})\text{C}(\text{O})]$, 92641-66-2; $[\text{Re}_2(\text{CO})_{10}]\text{C}(\text{O})\text{C}(\text{O})$ *neo*- $\text{C}_5\text{H}_{11}\text{Li}$ derivative, 92641-68-4; $\text{NaMn}(\text{CO})_5$, 13859-41-1; $\text{NaRe}(\text{CO})_5$, 33634-75-2; $\text{Re}_2(\text{CO})_{10}$, 14285-68-8; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; oxalyl chloride, 79-37-8.

Supplementary Material Available: Tables listing the anisotropic vibrational parameters and the observed and calculated structure factors (all structure determination calculations were carried out with programs of the Nicolet SHELXTL system on a Data General ECLIPSE (R) minicomputer; complex neutral atom scattering factors were taken from ref 24) (8 pages). Ordering information is given on any current masthead page.

$$(23) R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}, S = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$$

(24) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, United Kingdom, 1974; Vol. IV.

Potential Application of (1,3-Dithiol-2-ylidene)metal Complexes to the Synthesis of Tetrathiafulvalene Derivatives

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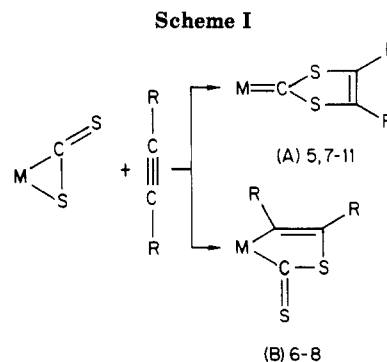
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1,3-Dithiol-2-ylidene derivatives are obtained by reacting hexafluorobut-2-yne with the $\eta^2\text{-CS}_2$ complexes (triphos)Ni($\eta^2\text{-CS}_2$) and (np₃)Ni($\eta^2\text{-CS}_2$). The 1,3-dithiolium carbene ligand can be easily replaced by CO and $\text{F}_3\text{CC}\equiv\text{CCF}_3$ and, in turn, dimerizes to tetrakis(trifluoromethyl)tetrathiafulvalene (CF_3 TTF). Some of the reactions reported present interesting catalytic aspects. The decomposition to air of the carbene complex (triphos)Ni[$\text{CS}_2\text{C}_2(\text{CF}_3)_2$] yields two dithiolene derivatives and CF_3 TTF.

Introduction

Much current interest is presently being shown in the chemistry of $\eta^2\text{-CS}_2$ metal complexes. These compounds, in fact, can serve as precursors for a variety of sulfur-containing ligands or free products.¹⁻¹²

A reaction of $\eta^2\text{-CS}_2$ complexes that could have interesting practical applications is the 1,3 dipolar cycloaddition of activated alkynes.⁵⁻¹¹ Depending on the nature of the metal fragment and of the coligands, alkynes can add to



$\text{M}-\eta^2\text{-CS}_2$ in two different ways (Scheme I).

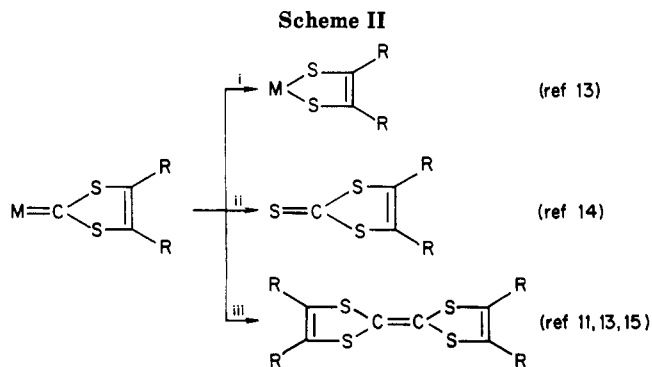
The potential applications of (1,3-dithiol-2-ylidene)metal derivatives of type A in the synthesis of sulfur-containing compounds appear to be very promising as shown in Scheme II.^{11,13-15}

- (1) Yanoff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.
- (2) Werner, H. *Coord. Chem. Rev.* **1982**, *43*, 165.
- (3) Bianchini, C.; Meli, A. *J. Chem. Soc., Chem. Commun.* **1983**, 156.
- (4) Schenk, W. A.; Schwietzke, T. *Organometallics* **1982**, *2*, 1905.
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- (6) Wakatsuki, Y.; Yamazaki, H.; Iwasaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 5781.
- (7) Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981**, *20*, 2486.
- (8) Le Bozec, H.; Gorgues, A.; Dixneuf, P. *J. Chem. Soc., Chem. Commun.* **1978**, 573.
- (9) Le Marouille, J. Y.; Lelay, C.; Benoit, A.; Grandjean, D.; Touchard, D.; Le Bozec, H.; Dixneuf, P. *J. Organomet. Chem.* **1980**, *191*, 133.
- (10) Frazier, C. C.; Magnussen, N. D.; Osuji, L. N.; Parker, K. O. *Organometallics* **1982**, *1*, 903.
- (11) Bianchini, C.; Meli, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1309.
- (12) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.*, in press.

(13) Carty, A. J.; Dixneuf, P. H.; Gorgues, A.; Hartstock, F.; Le Bozec, H.; Taylor, N. *J. Inorg. Chem.* **1981**, *20*, 3929.

(14) Ngounda, M.; Le Bozec, H.; Dixneuf, P. *J. Org. Chem.* **1982**, *47*, 4000.

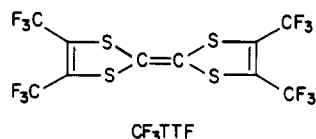
(15) Le Bozec, H.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1462.



Of the results presented in Scheme II, that at point iii is of particular interest. Tetrathiafulvalene (TTF) and its derivatives can act, in fact, as π donors in the preparations of organic charge-transfer salts having metallic properties.¹⁶ For this reason, increasing interest is directed toward the development of new routes to TTF derivatives.

We are actually trying to find metal-assisted syntheses of TTF derivatives, with the ultimate goal of achieving a catalytic route to these compounds.

Herein we report two facile generations of tetrakis(trifluoromethyl)tetrathiafulvalene (CF_3TTF) from $\eta^2\text{-CS}_2$ complexes. Both of these synthetic routes exhibit some interesting catalytic aspects.



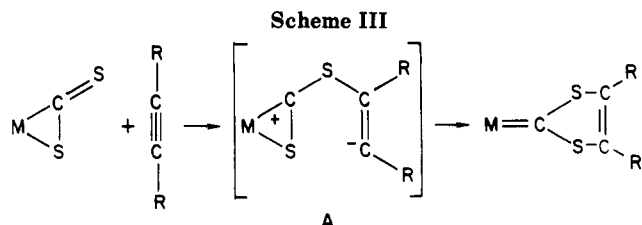
A preliminary account has been given of some of the results described in this paper.¹¹

Experimental Section

Unless stated otherwise, all reactions and manipulations were carried out at room temperature under a nitrogen atmosphere. THF and saturated hydrocarbon solvents were distilled from Na/benzophenone under nitrogen. Other solvents were used as obtained from commercial sources. Literature methods were used for the preparation of (triphos)Ni(CS_2)¹⁷ and (np_3)Ni.¹⁸ Hexafluorobut-2-yne and Ni(COD)₂ were purchased from Strem. The solid complexes were collected on a sintered-glass frit and washed with petroleum ether before being dried in a stream of nitrogen. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer using samples mullied in Nujol between KBr plates. ³¹P{¹H} NMR spectra were taken on a Varian CFT 20 spectrometer. Peak positions are relative to phosphoric acid, with downfield values reported as positive.

(triphos)Ni[CS₂C₂(CF₃)₂] (1). Hexafluorobut-2-yne (0.38 g, 2.3 mmol) was condensed on to a suspension of (triphos)Ni(CS_2) (1.5 g, 2 mmol) in THF (150 mL) (-196 °C). When the reaction mixture was allowed to warm to room temperature, the solid dissolved and a dark red solution was formed. After removal of the solvent under reduced pressure, pentane (20 mL) was added to the resulting red brown solid, which was then filtered off; yield 95%. Anal. Calcd for C₄₈H₃₆F₆NiP₃S₂: C, 59.95; H, 4.26; F, 12.37; Ni, 6.37; S, 6.95. Found: C, 59.77; H, 4.21; F, 12.23; Ni, 6.29; S, 6.87.

(triphos)Ni(F₃CC≡CCF₃) (3). Hexafluorobut-2-yne was bubbled through a THF (30 mL) solution of Ni(COD)₂ (0.27 g, 1 mmol) and triphos (0.62 g, 1 mmol) at 0 °C until the color



changed from orange to yellow. On concentration to ca. 10 mL at reduced pressure and addition of heptane (20 mL), 3 was obtained as yellow powder in 70% yield. Anal. Calcd for C₄₅H₃₆F₆NiP₃: C, 63.92; H, 4.65; Ni, 6.94; P, 10.99. Found: C, 63.88, H, 4.61; Ni, 6.88; P, 11.04.

Reaction of 1 with Hexafluorobut-2-yne. Hexafluorobut-2-yne was bubbled through a THF (30 mL) solution of 1 (0.46 g, 0.5 mmol) until the color turned light orange. The solvent was then removed in vacuo, and the residue was first washed with three 10-mL portions of pentane and then extracted with CH₂Cl₂ (15 mL). On addition of hexane (20 mL) 3 precipitated as yellow powder in 60% yield together with trace amounts of unidentified products which we did not succeed in separating from 3.¹⁹ The pentane layer was then concentrated to dryness and the residue sublimed at 60 °C (0.25 torr). Tetrakis(trifluoromethyl)tetrathiafulvalene (CF_3TTF)²⁰ was obtained in 50% yield.

Reaction of 1 with Carbon Monoxide. CO was slowly passed through a THF (30 mL) solution of 1 (0.46 g, 0.5 mmol) until the color changed from dark red to yellow orange (about 15 min). The resulting mixture was then worked up as described above to give both yellow crystals of (triphos)Ni(CO)²¹ (4) and CF_3TTF in 90 and 62% yields, respectively.

Reaction of (np_3)Ni with CS₂ and Hexafluorobut-2-yne. Variable amounts of F₃CC≡CCF₃ (4–8 mmol) were condensed on to a CS₂ (80 mL) solution of (np_3)Ni (0.71 g, 1 mmol). The reaction mixture was then allowed to warm to room temperature over 30 min. During this time a darkening of the color occurred. After removal of the solvent at reduced pressure the resulting brown residue was sublimed to give CF_3TTF in 150–200% yield. The remaining solid material was repeatedly analyzed. The data obtained were indicative of a mixture of products. IR: 3070 w, 1595 s, 1540 m, 1265 s, 1170 s, 1120 s, 1090 s, 1000 w cm⁻¹.

Exposition of 1 to Air. A solution of 1 (1.84 g, 2 mmol) in CH₂Cl₂ (100 mL) was exposed to air for 5–6 h. During this time the dark red starting color became orange-brown. The solvent was then removed in vacuo, and the residue was washed with five 30-mL portions of pentane before being extracted with CH₂Cl₂ and chromatographed in air on silica gel thick-layer plates (eluent CH₂Cl₂-methanol). The orange complexes (triphos)Ni[S₂C₂(CF₃)₂] (8) and (triphos=O)Ni[S₂C₂(CF₃)₂] (9) were isolated and crystallized from CH₂Cl₂-*n*-butyl ether mixtures in 27 and 18% yields, respectively. The pentane layer was concentrated to dryness and sublimed to give CF_3TTF in 18% yield.

Results and Discussion

It is generally accepted that the capability of η^2 -bonded carbon disulfide complexes to react with activated acetylenes is a consequence of the 1,3 dipolar character of the metal- $\eta^2\text{-CS}_2$ moiety.²² Most of the reactions reported in the literature lead to 1,3-dithiol-2-ylidene derivatives, with a mechanism which very likely implies an intermediate of type A (Scheme III).⁷

An analogous mechanism can be tentatively proposed for the formation of the (1,3-dithiol-2-ylidene)nickel complex, (triphos)Ni[CS₂C₂(CF₃)₂] (1) [triphos = 1,1,1-tris-[(diphenylphosphino)methyl]ethane], which is obtained by adding hexafluorobut-2-yne to a suspension of (trip-

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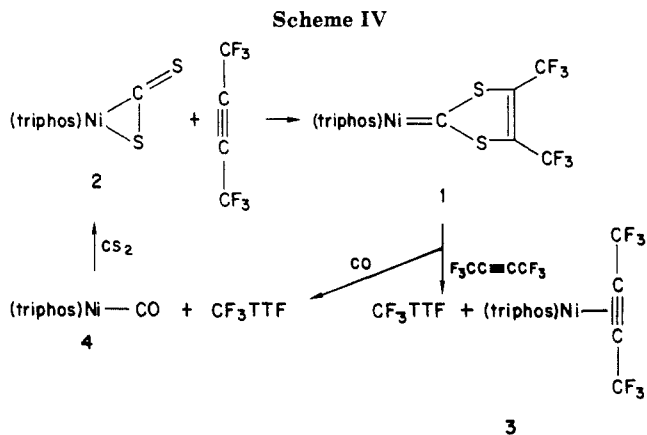
(18) Mealli, C.; Sacconi, L. *J. Chem. Soc., Chem. Commun.* **1973**, 886.

(19) The ³¹P{¹H} NMR spectrum (CDCl₃, -55 °C) contains two resonances at ca. 26 and 22 ppm assigned to side products.

(20) Hartzler, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 4379.

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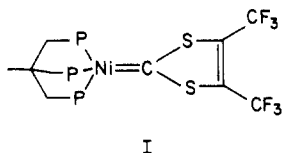
(22) Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *17*, 2568.



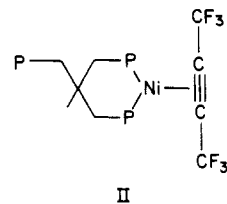
hos)Ni(η^2 -CS₂) (2) (Scheme IV).

Compound 1 is a diamagnetic red-brown solid, fairly stable both in the solid state and in solution in an inert atmosphere. The IR spectrum contains no ν (C=S) vibrations, but there are strong bands at 1250, 1165, and 1125 cm⁻¹, which can be assigned to C-F stretch.^{20,23,24} A medium band at 1585 cm⁻¹ is attributable to ν (C=C) for the F₃CC=CCF₃ moiety.^{20,24} The ³¹P{¹H} NMR spectrum (CDCl₃, 20 °C) consists of a single resonance at 8.24 ppm. This pattern does not vary with the temperature and is consistent with the rapid intramolecular exchange of the three phosphorus atoms of triphos around the nickel atom.²⁵

On the basis of analytical and spectroscopic data it is reasonable to assign to 1 the structure I, where the nickel atom is four-coordinated by triphos and by the 1,3-dithiol-2-ylidene ligand CS₂C₂(CF₃)₂.



Further support to the presence of a dithiocarbene ligand in 1 is provided by its reactivity toward F₃CC≡CCF₃ and CO. Addition of an excess of hexafluorobut-2-yne to a THF solution of 1 results, in fact, in the displacement of the 1,3-dithiolium carbene ligand with consequent formation of the diamagnetic yellow complex (triphos)Ni(π -F₃CC≡CCF₃) (3). The 1,3-dithiolium carbene in turn dimerizes to give tetrakis(trifluoromethyl)tetrathiafulvalene (CF₃TTF)²⁰ in 50% yield (Scheme IV). The structure of 3 has been ascertained by means of spectroscopic measurements. The IR spectrum with bands at 1790 (C≡C), 1265, 1230, and 1129 cm⁻¹ (CF) is comparable with those reported for other metal complexes containing triphos or different tertiary phosphines and π -bonded hexafluorobut-2-yne^{23,26} or tetrafluoroethylene.²⁷ The ³¹P{¹H} NMR spectra for the temperature range +30 to -55 °C have been recorded. At -55 °C the spectrum indicates a "frozen" structure, in which the triphos ligand is functioning as a bidentate ligand with one of the terminal PPh₂ groups unbonded. The most likely structure of the complex is illustrated in II. The ³¹P NMR assignments are



as follows: δ (P_{free}) -25.50, δ (P_{bonded}) 14.50 (δ (free triphos ligand) -25.0). As the temperature is raised, the bonded and free PPh₂ groups begin to exchange positions as evidenced by the simultaneous broadening of the above resonances. At +30 °C they give rise essentially to a broad absorption at ca. 5 ppm. The pattern of the bands as well as their temperature dependence are in line with those previously reported for other fluxional triphos complexes.²⁸ It is noteworthy that 3 can be synthesized directly by reaction of Ni(COD)₂ with hexafluorobut-2-yne in the presence of triphos.

The 1,3-dithiolium carbene ligand in 1 is easily replaced also by carbon monoxide. In this case, the formation of CF₃TTF in 62% yield is accompanied by that of yellow crystals of (triphos)Ni(CO)²¹ (4) (Scheme IV). Since the starting η^2 -CS₂ complex 2 can be easily regenerated by treatment of an acetone solution of 4 with CS₂^{28b} and since the direct synthesis of CF₃TTF from CS₂ and F₃CC≡CCF₃ requires more drastic reaction conditions with minor yields,²⁰ the present route to CF₃TTF could be considered a "catalytic" process where the (triphos)Ni moiety acts as a catalyst.

Interesting catalytic aspects can be envisaged also in the synthesis of CF₃TTF from CS₂ and F₃CC≡CCF₃ in the presence of the trigonal-pyramidal nickel(0) complex (np₃)Ni (5) [np₃ = tris[2-(diphenylphosphino)ethyl]amine]. The latter compound is known to react with CS₂ forming the complex (np₃)Ni(η^2 -CS₂) (6), where np₃ acts as a tridentate ligand with the nitrogen atom uncoordinated.²⁹ When a CS₂ solution of 5 is treated with hexafluorobut-2-yne, CF₃TTF is obtained in 150–200% yields. A reasonable reaction pathway for the formation of CF₃TTF is that involving the intermediacy of the (1,3-dithiol-2-ylidene) complex (np₃)Ni[CS₂C₂(CF₃)₂] (7), where np₃ behaves as a tridentate ligand with the nitrogen uncoordinated. The coordination of the latter donor atom to the metal should cause the expulsion of the 1,3-dithiolium carbene ligand, with consequent formation of the starting (np₃)Ni complex and dimerization of the carbene ligand to CF₃TTF (Scheme V). In CS₂ the regeneration of the η^2 -CS₂ complex 6 may then occur and another cycle follows. The low turnover observed may be attributed to competing reactions of 5, such as that with F₃CC≡CCF₃ to give a π -bonded complex as in the case with triphos. Indeed the elimination of CS₂ under reduced pressure gives a brown solid. In addition to the absorptions of CF₃TTF,²⁰ the IR spectrum of this material exhibits bands that are typical of the np₃ ligand, CF₃ groups, and >C=C< moieties. Identical composition and IR band pattern are observed for the brown powder that precipitates by adding to the (np₃)Ni-CS₂-F₃CC≡CCF₃ mixture a solvent like *n*-heptane where CF₃TTF is soluble. On the other hand, no CF₃TTF can be obtained by subliming this brown product. This fact suggests that the formation of CF₃TTF, and hence the decomposition of 7, are not related to the sub-

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(24) Krespan, C. G. *J. Am. Chem. Soc.* 1961, 83, 3434.

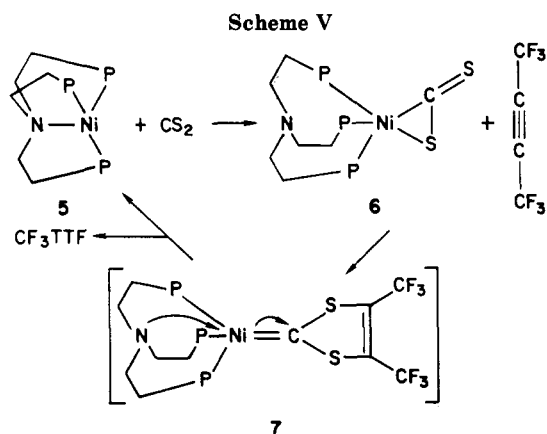
(25) The ³¹P NMR spectra of the tetrahedral (triphos)Ni(CO) and square-pyramidal (triphos)Ni(η^2 -CS₂) complexes consist of a single resonance at 11.82 (CDCl₃, 20 °C) and -4.41 ppm (CD₂Cl₂, 20 °C), respectively.

(26) Oztuka, S.; Nakamura, A. *Adv. Organomet. Chem.* 1976, 14, 245.

(27) Maples, P. R.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1973, 388.

(28) (a) Bianchini, C.; Mealli, C.; Meli, A.; Scapacci, G. *Organometallics* 1983, 2, 141. (b) Bianchini, C.; Innocenti, P.; Meli, A. *J. Chem. Soc., Dalton Trans.* 1983, 1777. (c) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* 1983, 2419.

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limation process. The presence of nickel, sulfur, fluorine, and the elements of np_3 is suggestive of a mixture of different products.

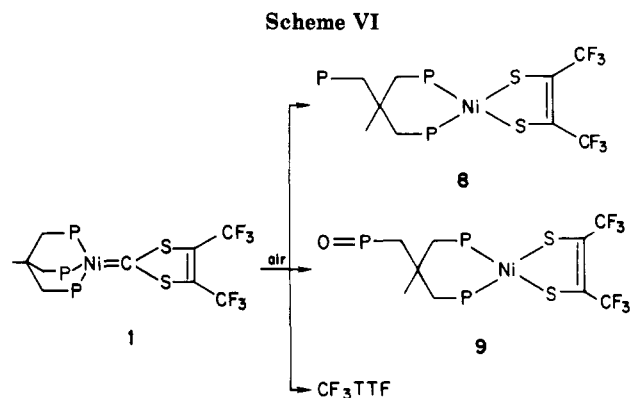
The very mild reaction conditions, the good yields, and the possibility of recycling the (triphos)Ni and (np_3) Ni moieties could make the present route to TTF derivatives preferable to some of the previously reported methods, which particularly for CF_3 TTF require drastic conditions. For instance, Hartzler has synthesized CF_3 TTF in 100% yield by heating CS_2 , $F_3CC\equiv CCF_3$, and CF_3CO_2H at 100 °C for 4 days.²⁰

To some extent the chemistry of the present (1,3-dithiol-2-ylidene)nickel complexes is unique. All of the reported metal complexes with analogous dithiocarbene ligands, in fact, are stable with respect to the displacement of the 1,3-dithiolium carbene by other ligands.^{7,9,10} Some of them are air-stable even in solution.^{9,10} The (1,3-dithiol-2-ylidene)iron complexes reported by Dixneuf⁷ seem to be the only compounds displaying some chemical analogies with our nickel compounds. In particular, the iron complexes produce TTF derivatives in good yields either by addition of iodine or by thermolysis but fail to give TTF when treated with CO .¹⁵ As for the thermolytic reaction, the authors suggest that the dimerization of the carbene ligand requires a vacant coordination site on the metal atom. Such a mechanistic consideration could be extended also to the CF_3 TTF generation herein reported, in the light of the fluxional behavior often shown by (triphos)metal complexes.

By contrast, Dixneuf's and our 1,3-dithiol-2-ylidene complexes exhibit very similar behavior when exposed to air, that is they decompose to dithiolene derivatives.

On exposition of a solution of 1 to air, the color changes from red to orange-brown within 5–6 h. The elimination of the solvent affords an orange-brown solid, from which CF_3 TTF can be isolated in 18% yield by sublimation. By chromatography of the remaining material on thick-layer silica gel plates, two products as orange crystals are then obtained. The latter compounds have been uniquely identified by means of IR and NMR spectroscopy as (dithiolene)nickel complexes of formula (triphos)Ni[$S_2C_2(CF_3)_2$] (8) and (triphos=O)Ni[$S_2C_2(CF_3)_2$] (9) [triphos=O = $O=PPh_2CH_2C(CH_3)(CH_2PPh_2)_2$], respectively (Scheme VI).

Compounds 8 and 9 are diamagnetic and fairly air-stable both in the solid state and in solution. They are soluble in common organic solvents, in which they behave as nonelectrolytes. The reflectance spectra, with no bands



at frequencies greater than $15\,000\text{ cm}^{-1}$, are typical of square-planar nickel(II) complexes.³⁰ The IR spectra are almost superimposable except in the region of phosphine oxides, where 9 shows absorptions at 1190, 1120, 580, and 570 cm^{-1} characteristic of $P=O$ groups.^{31,32} Bands at 1255, 1165, 1130 ($\nu(C-F)$), and 1555 cm^{-1} ($\nu(C=C)$) are present in both spectra. The $^{31}P\{^1H\}$ NMR spectrum of 8 ($CDCl_3$, 20 °C) consists of two resonances at 13.57 and -27.87 ppm (intensity ratio 2:1), which, by comparison with other (triphos)metal complexes, can be positively assigned to triphos acting as a bidentate ligand (13.57 ppm) with the third phosphorus atom uncoordinated (-27.87 ppm).²⁸ The $^{31}P\{^1H\}$ NMR spectrum of 9 ($CDCl_3$, 20 °C) shows two resonances at 26.21 and 13.60 ppm (intensity ratio 1:2). This pattern is consistent with the presence of the triphos=O ligand acting as a bidentate ligand through the two phosphine donor atoms.³² The easy oxidation of a phosphine arm of triphos to $P=O$ has been already observed for a number of metal complexes with triphos acting as a bidentate ligand.^{31,32} Thus, it is not surprising that 8, even though very slowly, converts to 9 when its solutions are exposed to air.

Considering the reaction mechanism for the decomposition of (1,3-dithiol-2-ylidene)metal complexes to dithiolene derivatives, we can add nothing to the proposals presented by Dixneuf in his paper.¹³ However, we agree that the intermediacy of bis(trifluoromethyl)dithiete appears very reasonable. The latter compound, in fact, is known to react with metal fragments to give dithiolene complexes.³³

The present synthesis of 8 and 9 further confirms that the reaction of activated acetylenes with η^2-CS_2 complexes represents a potentially useful route to dithiolene derivatives.

We are presently trying to extend the reactions herein reported to other activated alkynes. Although the separation of the reaction products is somewhat difficult, encouraging results have been obtained with dimethyl acetylenedicarboxylate.

Registry No. 1, 89952-75-0; 2, 60294-99-7; 3, 89952-76-1; 4, 14876-51-8; 5, 52633-73-5; 6, 92545-25-0; 8, 92545-26-1; 9, 92545-27-2; CF_3 TTF, 26393-26-0; Ni(COD)₂, 1295-35-8; $F_3CC\equiv CCF_3$, 692-50-2.

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