New Metal-assisted Synthesis of Tetrakis(trifluoromethyl)tetrathiafulvalene

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Replacement of the 1,3-dithiolium carbene ligand by CO or $F_3CC{\equiv}CCF_3$ in the complex [(triphos)Ni{$CS_2C_2(CF_3)_2$}] [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] affords the complexes [(triphos)Ni(CO)] or [(triphos)Ni($F_3CC{\equiv}CCF_3$)], whereas the 1,3-dithiolium carbene dimerizes to tetrakis(trifluoromethyl)tetrathiafulvalene.

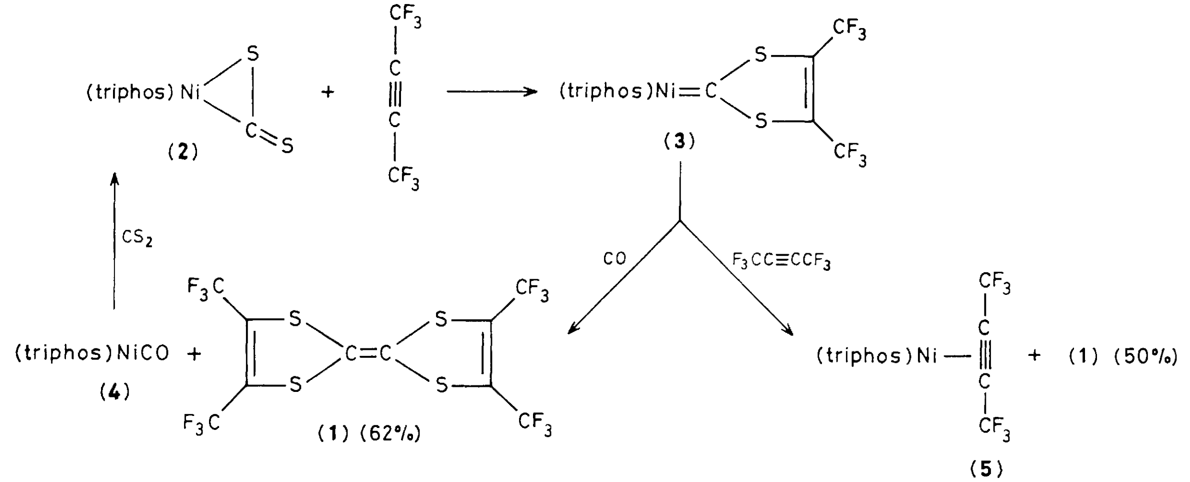
Since the discovery that tetrathiafulvalene (TTF) and its derivatives can act as π donors in the preparations of organic charge-transfer salts having metallic properties,[1] increasing attention has been directed to their synthesis by both organic and organometallic chemists. A number of synthetic routes are now available,[2] including some metal-promoted reactions.[3]

We report here a new and efficient synthesis of the known tetrakis(trifluoromethyl)tetrathiafulvalene (**1**) through a procedure whose individual steps are unusual and significant examples of organometallic chemistry (Scheme 1).

On allowing a tetrahydrofuran (THF) solution of the complex [(triphos)Ni(η^2-CS_2)][4] (**2**) [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane] to react with a slight excess of hexafluorobut-2-yne at 0 °C, a dark red solution results. Elimination of the solvent under reduced pressure gives the (1,3-dithiol-2-ylidene)nickel complex [(triphos)Ni{$CS_2C_2(CF_3)_2$}][†] (**3**), as a red brown solid in 95% yield.

Addition of carbon monoxide to a THF solution of (**3**) at room temperature results in the displacement of the 1,3-dithiolium carbene ligand with consequent formation of yellow crystals of the complex [(triphos)Ni(CO)][5] (**4**). The 1,3-dithiolium carbene in turn dimerizes to give the tetrathiafulvalene (**1**) in 62% yield.

[†] Satisfactory elemental analytical data were obtained; i.r. (Nujol): 1585(C=C), 1250, 1165, 1125 cm^{-1} (CF); ^{31}P{^{1}H} n.m.r. ($CDCl_3$, 20 °C): 8.24 p.p.m. (s), this pattern is consistent with rapid intramolecular exchange of the three phosphorus atoms of triphos around the nickel atom. The complex is fairly stable both in the solid state and in solution in an inert atmosphere.



Scheme 1

Since the starting η^2-CS_2 complex (**2**) can be easily regenerated by treatment of an acetone solution of (**4**) with CS_2, and since the direct synthesis of (**1**) from CS_2 and $F_3CC{\equiv}CCF_3$ requires more drastic reaction conditions with minor yields,[6] the present route to (**1**) could be considered a 'catalytic' process where the (triphos)Ni moiety acts as the catalyst.

Alternatively, TTF derivative (**1**) can be synthesized in 50% yield by reaction of a THF solution of (**3**) with a large excess of hexafluorobut-2-yne. In this case, the 1,3-dithiolium carbene is replaced by a π-bonded alkyne molecule to form the yellow complex $[(\text{triphos})Ni(\pi\text{-}F_3CC{\equiv}CCF_3)]$‡ (**5**), where triphos acts as a bidentate ligand with an unco-ordinated phosphorus atom.

The very mild reaction conditions, the good yields, and the possibility of recycling the (triphos)Ni moiety could make the present route to TTF derivatives preferable to some of the previously reported methods, which particularly for (**1**), require drastic conditions (Carius tube, 100 °C, 4 days), giving yields below 50%.

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References

1 L. B. Collman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, and A. G. Garito, *Solid State Commun.*, 1973, **12**, 1125; J. P. Ferraris, D. O. Cowan, V. Waletka, and J. H. Perlstein, *J. Am. Chem. Soc.*, 1979, **95**, 948.
2 M. Narita and C. H. Pittman, Jr., *Synthesis*, 1976, 489; M. Mizuno, A. F. Garito, and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1978, 18; A. Gorgues, P. Batoil, and A. Le Coq, *ibid.*, 1983, 405.
3 H. Le Bozec, A. Gorgues, and P. H. Dixneuf, *Inorg. Chem.*, 1981, **20**, 2486.
4 P. Dapporto, S. Midollini, A. Orlandini, and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 2768.
5 J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1965, 812.
6 H. D. Hartzler, *J. Am. Chem. Soc.*, 1973, **95**, 4379.
7 S. Otzuka and A. Nakamura, *Adv. Organomet. Chem.*, 1976, **14**, 245.
8 P. K. Maples, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1973, 388.
9 C. Bianchini, C. Mealli, A. Meli, and G. Scapacci, *Organometallics*, 1983, **2**, 141; C. Bianchini, P. Innocenti, and A. Meli, *J. Chem. Soc., Dalton Trans.*, 1983, 1777.

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‡ Satisfactory analytical data could not be obtained since (**5**) is always accompanied by some side-products, which so far we have not succeeded in separating from (**5**). However, the given structural formulation is strongly supported by its spectroscopic data, which agree with those reported for other metal complexes containing triphos or different tertiary phosphines and π-bonded hexafluorobut-2-yne[7] or tetrafluoroethylene.[8] Moreover (**5**) can be synthesized directly by reaction of $Ni(cod)_2$ (cod = cyclo-octa-1,5-diene) with hexafluorobut-2-yne in the presence of triphos: i.r. (Nujol): 1790 (C≡C), 1265, 1230, and 1129 cm^{-1} (CF); $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): together with signals at *ca.* 26 and 22 p.p.m. which we assign to side products; the spectrum at −55 °C shows two signals at 14.50 and −25.50 p.p.m. At 30 °C these two bands disappear, whereas a broad band at *ca.* 5 p.p.m. is present. The pattern of the bands as well as their temperature-dependence are in line with those previously reported for other fluxional triphos complexes.[9]