Journal of Organometallic Chemistry, 236 (1982) C75—C77
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

CYCLOADDITION OF DIMETHYLACETYLENE DICARBOXYLATE TO η^2-COORDINATED TRITHIOCARBONATE

CLAUDIO BIANCHINI and ANDREA MELI

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del C.N.R., Via Guerrazzi 27, 50132 Florence (Italy)

(Received June 4th, 1982)

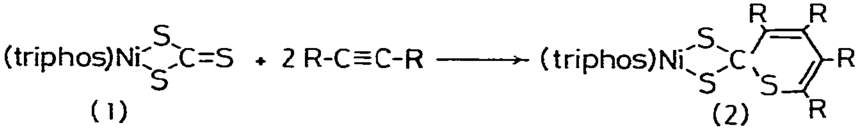
Summary

The reaction of the η^2-trithiocarbonate complex $[(\text{triphos})\text{Ni}(\text{S}_2\text{CS})]$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) with dimethylacetylene dicarboxylate gives the nickel(II) complex $[(\text{triphos})\text{Ni}(\text{S}_2{=}\overline{\text{CSCR=CRCR=C}}\text{R})]$ ($\text{R} = \text{CO}_2\text{CH}_3$) containing as ligand an unprecedented 2,2 dithiolato derivative of substituted thiapyran.

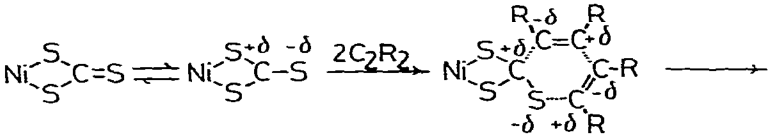
It has recently been shown that η^2-CS_3 metal complexes can be conveniently used as nucleophilic agents. Reactions of the η^2-CS_3 group include alkylation at the uncoordinated sulfur atom [1,2], formation of dinuclear complexes containing a trithiocarbonate bridging group [1,2], and abstraction of sulfur to give carbon disulfide complexes [3].

We have found that the addition of the trithiocarbonato ion to the metal generates two potentially reactive sites, the uncoordinated sulfur atom and the carbon atom, susceptible to attack by electrophilic and nucleophilic agents, respectively.

A tetrahydrofuran solution of $[(\text{triphos})\text{Ni}(\text{S}_2\text{CS})]$ (1), (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) reacted at room temperature under an inert atmosphere with 2 equiv. of dimethylacetylene dicarboxylate, to give a solution from which orange crystals of 2 were obtained in good yield.

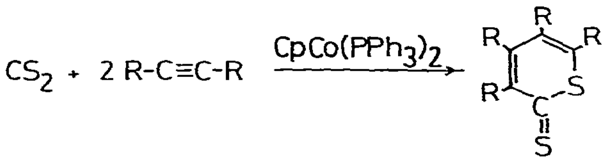


Complex 2 is diamagnetic, and air stable in the solid state. It is moderately soluble in chlorinated solvents, in which it behaves as a non-electrolyte. Dimethylacetylene dicarboxylate is known to react with η^2-CS_2 metal complexes to give heterocyclic five-membered metallo-ring derivatives [4,5]. The analytical and spectroscopic data by complex 2 rule out a metallo-ring formulation, but instead support the 1,1-dithiolate structure 2. The ^1H NMR spectrum of a chloroform solution of 2 at room temperature shows the presence of three different types of carbomethoxy protons at δ 3.61, 3.45, and 3.28 ppm (intensity ratio 1/2/1), thus indicating that two dimethylacetylene dicarboxylate molecules participate in the reaction. The chemical shifts and the intensities of the signals provide support for the proposed structure 2. The IR spectrum, as a Nujol mull, lends further confirmation to this formulation. Two infrared absorptions in the C=O stretching region at 1715, and 1685 cm^{-1} agree well with those found for other heterocycles containing CO_2CH_3 substituents [4,5]. A band at 1630 cm^{-1} is attributable to ν(C=C) for the cycloalkene moiety. Finally, a strong infrared absorption at 1020 cm^{-1} may be attributed to a C=S stretch. This band is at lower frequency than that of most thiones, and thioesters, and in particular, than that of the starting dithiocarbonate complex (1045 cm^{-1}) suggesting that there may be some delocalization over the $S(CR)_4$ portion of the heterocyclic ring.



(2)

A variety of reactions paths may be proposed to explain the formation of complex 2. One of the more probable mechanisms, proceeding by one-step cycloaddition, is shown, in which the trithiocarbonate ligand behaves as a 1,2-dipolarophile. The formation of the $[S_2{=}\overline{CSCR{=}CRCR{=}C}R]^{2-}$ ligand from the reaction of 1 with dimethylacetylene dicarboxylate has a close analogy in the catalyzed syntheses of substituted α-dithiopyrones from activated acetylenes and CS_2 [6].



These studies suggest that potential ligand transformations could provide new organic heterocyclic compounds.

Acknowledgments. Thanks are expressed to Mr. G. Scapacci and Mr. F. Cecconi for technical assistance.

References

1 C. Bianchini, C. Mealli, A. Meli and G. Scapacci, *J. Chem. Soc.*, Dalton Trans., (1982) 799.
2 I.B. Benson, J. Hunt, S.A.R. Knox and V. Oliphant, J. Chem. Soc., Dalton Trans., (1978) 1240.
3 C. Bianchini and A. Meli, unpublished results.
4 A.J. Carty, P.H. Dixneuf, A. Gorgues, F. Hartstock, H. Le Bozec and H.J. Taylor, Inorg. Chem., 20 (1981) 3829 and ref. therein.
5 J.Y. Le Marouille, C. Lelay, A. Benoit, D. Grandjean, D. Touchard, H. Le Bozec and P. Dixneuf, J. Organometal. Chem., 191 (1980) 133.
6 Y. Wakatsuki and H. Yamazaki, Tetrahedron Lett., (1974) 4549 and ref. therein.