
Selective Synthesis of Seven-membered Cyclic Thione Analogues of Acid Anhydrides and Other Related Derivatives *via* a Benzannelated Nickelacycle

Juan Cámpora, Ernesto Carmona,* Pilar Palma, and Manuel L. Poveda

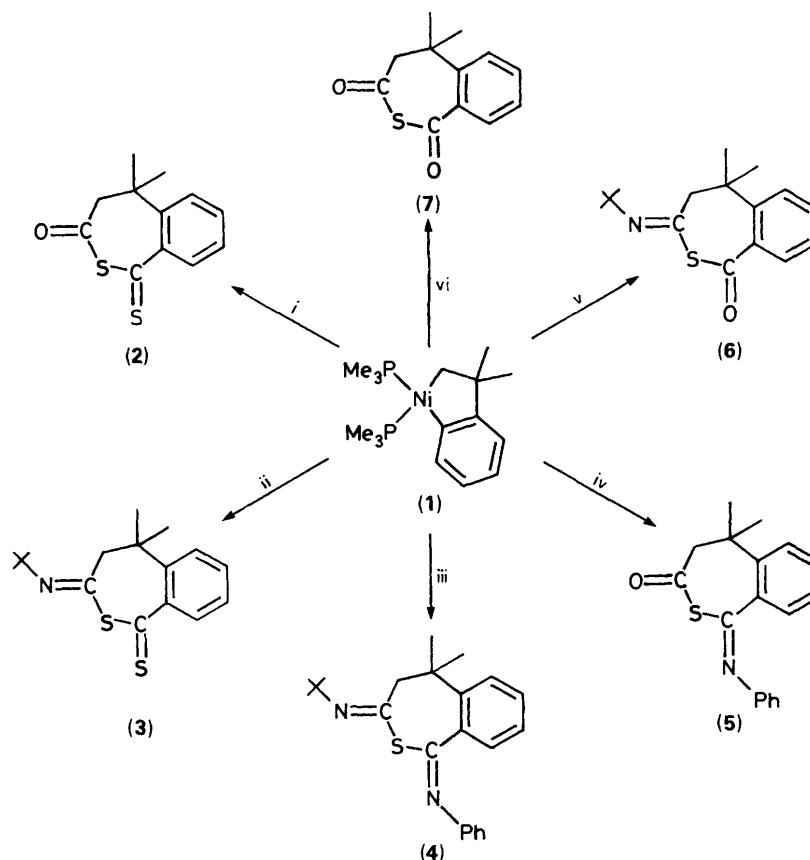
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales, Universidad de Sevilla-CSIC, Apdo. 553 41071 Sevilla, Spain.

The ready available benzonickelacyclopentene complex $(\text{Me}_3\text{P})_2\overline{\text{Ni}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)}$ (**1**) has been used to prepare a series of seven-membered ring thione analogues of acid anhydrides and other related derivatives through regioselective sequential insertion reactions of selected unsaturated molecules (CS_2 , COS, SCNPh, CO, CNBu^t) into the Ni-C bonds.

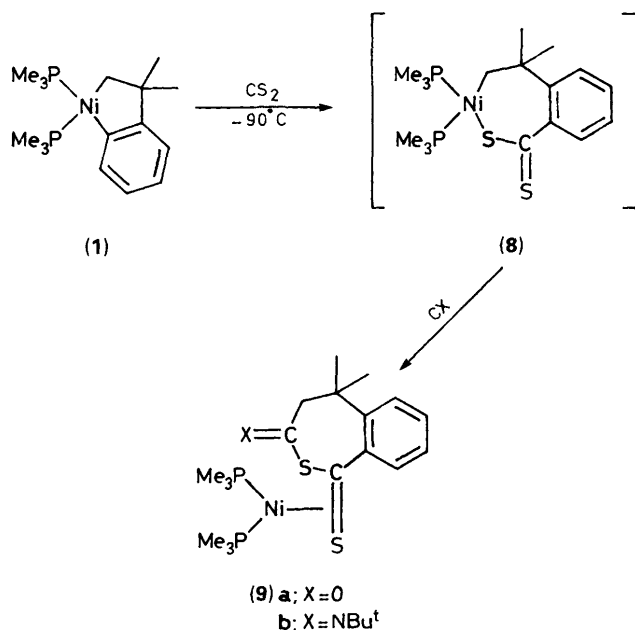
The synthesis of heterocycles with organometallic reagents has attracted wide interest.¹ We have shown recently that the benzannelated nickelacyclopentene complex (**1**) readily undergoes insertion reactions with unsaturated molecules such as CO, CO₂, or CS₂ to yield lactones, dithiolactones, ketones, or thioketones among others.² Here we further explore the reactivity of (**1**) and apply it to the synthesis of thione analogues of acid anhydrides and to related imine derivatives as shown in the Scheme. The thione analogues of acid anhydrides are compounds of considerable interest^{3a} and although some stable derivatives have been prepared recently, they are in general rather unstable and elusive molecules.³ The synthetic approach

used herein relies on the regioselective insertion of heterocumulenes CS₂, COS and SCNPh into the Ni-aryl bond of (**1**), to yield reactive intermediates able to undergo additional insertion of CO and CNBu^t into the Ni-alkyl bond. Compound (**1**) rapidly reacts with 1 equiv. of CS₂, at -90 °C, to give the proposed intermediate (**8**),[†] that converts into the isolable complexes (**9a**) or (**9b**) by additional insertion of CO or CNBu^t

[†] All attempts to isolate this species were frustrated by its irreversible rearrangement to the isomeric dithiolactone Ni(0) complex $(\text{Me}_3\text{P})_2\text{-Ni}(\eta^2\text{-S}=\overline{\text{C-S-CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4})$. See reference 2b.



Scheme. Reagents and conditions: *i*, (a) CS_2 , -90°C , (b) CO , -90°C to r.t., (c) dmpe , r.t., (d) Br_2 , THF , -90°C ; *ii*, as for *i* except (b) CNBu^t , -90°C to r.t.; *iii*, (a) PhNCS , -50°C , (b) CNBu^t , -50°C to r.t., (c) CO , THF , r.t.; *iv*, (a) PhNCS , -50°C , (b) CO , -50°C to r.t.; *v*, (a) COS , -90°C , (b) CNBu^t , -90°C to r.t., (c) CO r.t.; *vi*, (a) COS , -90°C , (b) CO , -90°C to r.t. All the reactions were carried out in Et_2O , unless otherwise indicated. Isolated yields are in the 60–90% range.



respectively. The acyl thioacyl sulphide (2) and the imino thioacyl sulphide (3) can be cleanly liberated by first replacing the PMe_3 ligands in (9a,b) by dmpe ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) and then oxidizing the resulting complexes with the stoichiometric amount of Br_2 at -90°C ,

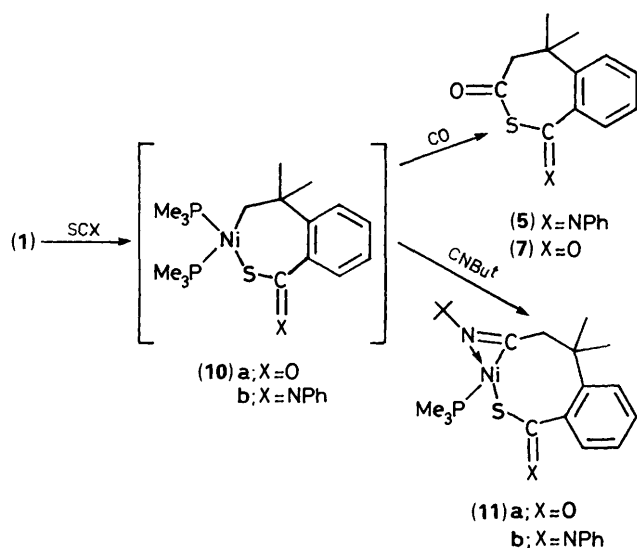
the sparingly soluble $\text{NiBr}_2(\text{dmpe})$ precipitating out of the solution.

Carbonyl sulphide (COS) and phenyl isothiocyanate (SCNPh) also insert into the Ni-aryl bond of (1) in a regioselective manner to produce thermally unstable, sulphur containing metallacycles of probable structure (10). Sequential insertion of CO at low temperatures induces a fast reductive elimination process that yields the bis(acyl) sulphide (7) or the imine acyl sulphide (5), starting from (10a) or (10b) respectively. Further evidence for the proposed intermediates (10) comes from the isolation of the η^2 -iminoacyls (11a) and (11b) by additional insertion of CNBu^t .⁴ Action of carbon monoxide on compounds (11a) and (11b) produces the imine acyl sulphide (6) and the bis(imine) sulphide (4) respectively, in high yields.

In summary, we have shown that sequential insertion reactions of unsaturated molecules into the Ni-C bonds of metallacycle (1) are of considerable utility for the synthesis of sulphur-containing heterocycles. Further studies aimed to ascertain the generality of this reaction pattern and to extend it to other related systems are in progress.

Experimental

Synthesis of (5).—To a stirred solution (-50°C) of $(\text{Me}_3\text{P})_2\text{Ni}(\text{CH}_2\text{CMe}_2\text{-o-C}_6\text{H}_4)$, (1), in diethyl ether (343 mg, 1 mmol, 20 ml) was added 1 equiv. of SCNPh (1 ml of a 1M solution in toluene). After 5 min of reaction CO was bubbled through the solution and the reaction mixture allowed to reach room temperature while gently flushing the flask with CO . The solvent was removed under reduced pressure and the residue



extracted with 20 ml of light petroleum (b.p. 40–60 °C). Filtration, concentration and cooling at -30°C afforded compound (5) as colourless crystals. Yield 93%, m.p. 130 °C (Found: C, 72.89; H, 5.87; N, 4.64. $\text{C}_{18}\text{H}_{17}\text{ONS}$ requires C, 73.22; H, 5.76; N, 4.64); M^+ , 283; ν_{max} (Nujol) 1 675 (C=O) and 1 580 (C=N) cm^{-1} ; δ_{H} (CDCl_3) 3.3 (s, CH_2) and 1.6 (s, CH_3); δ_{C}

(CDCl_3) 32.2 (CMe_2), 38.9 (CMe_2), 57.5 (CH_2), 119.7, 126.8, 128.3, 129.0, 129.2, 130.4, 130.7 (2:1:1:1:2:1:1 ratio, C–H aromatics), 139.3, 144.4, 149.5 (quaternary aromatics), 157.5 (C=NPh), and 195.2 (C=O).

Acknowledgements

This work is supported by the Dirección General de Política Científica through Grant PB 86–0653.

References

- (a) J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, 'Principles and Applications of Organotransition Metal Chemistry,' 2nd edit., University Science Books, Mill Valley, CA, USA, 1987; (b) S. G. Davies, 'Organotransition Metal Chemistry: Applications to Organic Synthesis,' Pergamon Press, Oxford 1982.
- (a) E. Carmona, E. Gutiérrez-Puebla, J. M. Marín, A. Monge, M. Paneque, M. L. Poveda, and C. Ruiz, *J. Am. Chem. Soc.*, 1989, **111**, 2883; (b) J. Cámpora, E. Carmona, E. Gutiérrez-Puebla, C. Ruiz, and M. L. Poveda, *Organometallics*, 1988, **7**, 2577.
- (a) M. V. Lakshmikantham, P. Carroll, G. Furst, M. I. Levinson, and M. Cava, *J. Am. Chem. Soc.*, 1984, **106**, 6084; (b) S. Yoneda, K. Ozaki, K. Yangi, and M. Minobe, *J. Chem. Soc., Chem. Commun.*, 1986, 19.
- L. D. Durfee and I. A. Rothwell, *Chem. Rev.*, 1988, **88**, 1059.

Paper 9/03878G

Received 22nd June 1989

Accepted 12th September 1989