Oxidative Addition of Aryl Sulphides to Low-valent Nickel Species

Ernest Wenkert,*[a] Michele E. Shepard,[a] and Andrew T. McPhail*[b]

[a] *Department of Chemistry, University of California-San Diego, La Jolla, CA 92093, U.S.A.*

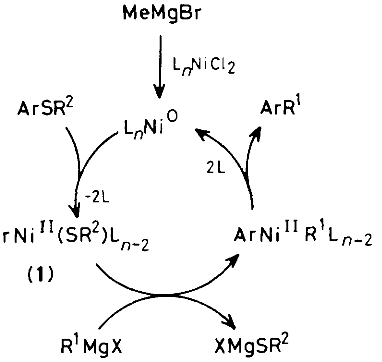
[b] *Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, NC 27706, U.S.A.*

Exposure of diaryl sulphides to tris(tri-n-butyl)phosphinonickel(0) is shown to lead to oxidative addition products, one of which has been characterized by n.m.r. spectral analysis and another by single-crystal *X*-ray analysis.

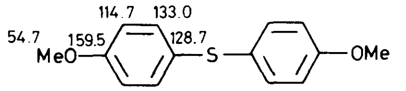
The reaction between Grignard reagents and aryl or alkenyl sulphides, catalysed by low-valent nickel species, has served as a facile method of synthesis of alkylarenes, biaryls, and alkenes in recent years.[1] Whereas the reactions were assumed to operate on the basis of the catalytic cycle depicted in Scheme 1,[2] no intermediates had ever been observed. This communication presents n.m.r. spectral data on an oxidative addition product of type (**1**) and the isolation and structure elucidation of another such compound.

Addition of a hexane solution of tris(tri-n-butyl)phosphinonickel(0), prepared by the method of Aresta *et al.*,[3] to a hexane solution of an equimolar quantity of di-*p*-methoxyphenyl sulphide (**2**) at −78 °C under argon in a Schlenk tube and the mixture then being permitted to warm to ambient temperature led to a solution of complex (**3**), as shown by ^{31}P and ^{13}C n.m.r. spectroscopy. A singlet in the ^{31}P n.m.r. spectrum at 6 p.p.m. (85% phosphoric acid as external standard) in contrast with a value of −28 p.p.m. for unbound tri-n-butylphosphine in hexane solution, indicated that the phosphines are ligated to nickel. The ^{13}C n.m.r. chemical shifts (shown on the formulae) reveal the change of structure undergone by the starting sulphide, the multiplicity of the nickel-attached carbon (a 10 Hz triplet due to a two-bond carbon–phosphorus coupling) indicating its *cis* relationship to two equivalent phosphine ligands.

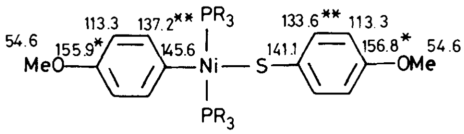
Since neither complex (**3**) nor related substances could be isolated and purified without decomposition, the preparation of a highly fluorinated complex was attempted. When an experiment as above was carried out on bis(pentafluorophenyl) sulphide, it resulted in the formation of an isolable, crystalline complex (**4**).† The structure of this product was defined by a single-crystal *X*-ray analysis which constitutes the first complete characterization of a nickel-insertion product of a carbon–sulphur bond system.‡



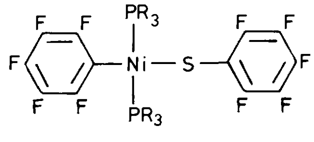
Scheme 1. R^1, R^2 = alkyl or aryl.



(**2**)



(**3**) R = Bu^n



(**4**) R = Bu^n

The numbers on the formulae are the ^{13}C n.m.r. chemical shift values. Asterisked values may be interchanged.

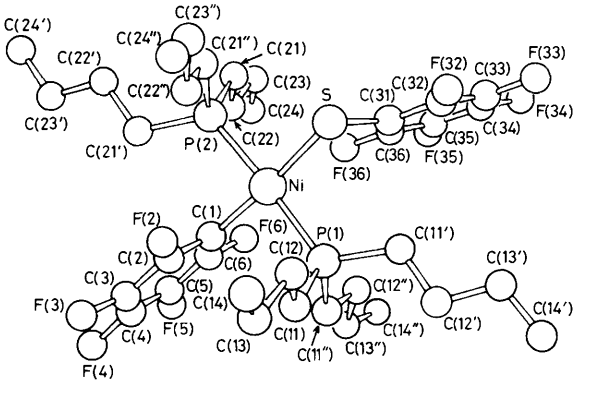


Figure 1. Molecular structure of *trans*-{Ni[P(Bu^n)$_3$]$_2$(C$_6$F$_5$S)(C$_6$F$_5$)} (**4**). Selected distances (Å) and angles (°) are: Ni–P(1) 2.241(2), Ni–P(2) 2.231(2), Ni–S 2.232(2), Ni–C(1) 1.918(5); P(1)–Ni–P(2) 175.90(7), P(1)–Ni–S 94.56(6), P(1)–Ni–C(1) 88.5(2), P(2)–Ni–S 86.45(6), P(2)–Ni–C(1) 90.0(1), S–Ni–C(1) 173.0(2), Ni–S–C(31) 112.3(2), S–C(31)–C(32) 120.4(5), S–C(31)–C(36) 125.9(4).

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† In quantitative yield (by ^{31}P n.m.r. spectral analysis). The compound was purified by chromatography on neutral alumina and elution with hexane, both at −78 °C under argon.

‡ The intermediacy of organonickel substances of type (**1**) in the Grignard reactions[1] is illustrated by the formation of *p*-t-butyltoluene (50% yield) on exposure of methylmagnesium bromide to the product of oxidative addition of the low-valent nickel species (prepared in the above manner) to *p*-t-butylthioanisole (E. Wenkert and J. M. Hanna, Jr., unpublished observation).

The molecular structure of (**4**) is illustrated in Figure 1.§ The square planar co-ordination geometry at nickel is distorted somewhat to accommodate non-bonded intramolecular interactions involving the sulphur-linked pentafluorophenyl ring. Thus, whereas the C(1)—C(6) ring is approximately orthogonal to the S–P(1)–P(2)–C(1) plane (dihedral angle 84.8°) with *ortho*-F · · · Ni distances of 3.11 and 3.14 Å, a similar F(36) · · · Ni separation of 3.06 Å is attained principally *via* bond angle deformation at Ni, S, C(31) accompanied by rotation about the S–C(31) bond [torsion angle Ni–S–C(31)–C(36) 31.6°].

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§ *Crystal data:* $C_{36}H_{54}F_{10}NiP_2S$ (**4**), $M = 829.54$, triclinic, space group $P\bar{1}$, $a = 13.782(3)$, $b = 14.644(3)$, $c = 12.353(3)$ Å, $\alpha = 111.84(2)$, $\beta = 113.53(2)$, $\gamma = 79.75(2)°$, $U = 2120.5$ Å^3, $Z = 2$, $D_c = 1.299$ g cm^{-3}. The crystal structure was solved by the heavy-atom approach. Full-matrix least-squares refinement of atomic positional and thermal parameters (anisotropic C, F, Ni, P, and S; fixed H contributions) converged at $R = 0.048$ [$R_w = 0.064$; $w = 1/\sigma^2(|F_o|)$] over 2980 absorption-corrected reflections [$I > 3.0\sigma(I)$] recorded on an Enraf–Nonius CAD-4 diffractometer (Cu-K_α radiation, $\lambda = 1.5418$ Å; incident-beam graphite monochromator; ω—2θ scans, $\theta_{max.}$ 67°). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

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2 Instead of the $Ni^0 \rightleftharpoons Ni^{II}$ ox–red equilibrium being the basis of the catalytic cycle, a $Ni^I \rightleftharpoons Ni^{III}$ interconversion may be operative, *cf.* T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 7547.

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