

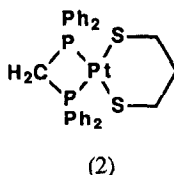
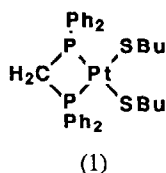
CARBON-SULPHUR BOND FORMATION CATALYSED BY BIS(DIPHENYLPHOSPHINO)-METHANE COMPLEXES OF PLATINUM (II)

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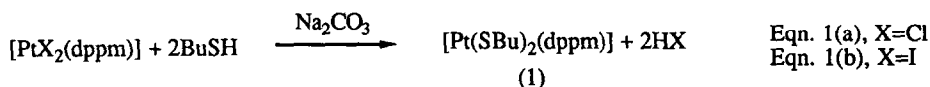
Summary: Thiols react with alkyl halides in the presence of sodium carbonate and a catalytic quantity of $(\text{dppm})\text{PtCl}_2$ to give thioethers. Of especial interest is the successful application to thioacetal formation using 1,1-dihalides, which does not require the use of strong bases or the intermediacy of thiolate anions.

The formation of bis(thiolate)platinum(II) complexes, e.g. $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{SR})_2]$ ($\text{R} = n\text{Pr}, i\text{Pr}, \text{CH}_2\text{Ph}$), by reaction of $[(\text{Ph}_3\text{P})_2\text{PtCl}_2]$ with thiols has been shown by Lai and Shaver to occur readily when carried out in the presence of the weak base triethylamine.¹ We recently prepared the bis(diphenylphosphino)methane (dppm) complex (1) by a similar route using sodium carbonate as the weak base (equation 1) and observed that it reacts readily with butyl iodide to give dibutyl sulphide (equation 2).





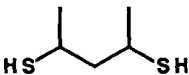
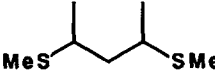




Equations 1(b) and 2 represent the catalytic formation of dibutylsulphide from butane thiol, butyl iodide, and weak base, since $[\text{PtI}_2(\text{dppm})]$ is regenerated. Further experiments showed that this carbon-sulphur bond forming reaction can readily be achieved in the presence of catalytic

amounts of [PtI₂(dppm)] or [PtCl₂(dppm)]. In the absence of complex, sodium carbonate does not mediate any reaction between alkane thiols and alkyl iodides in boiling acetone solution.²



The overall reaction is quite general and proceeds rapidly and in high yield (Table). The reaction is remarkably clean and is easy to carry out. In a typical experiment the reagents are mixed and boiled in acetone or methanol solution overnight. The solvent is removed, the residue extracted with ether, and the ethereal solution filtered and evaporated to dryness to yield the sulphide, usually requiring no further purification. As would be expected for simple nucleophilic substitution, the reactions proceed most efficiently for iodides and bromides (entries 1-4, 6, 7), chlorides being poor substrates (entry 8).

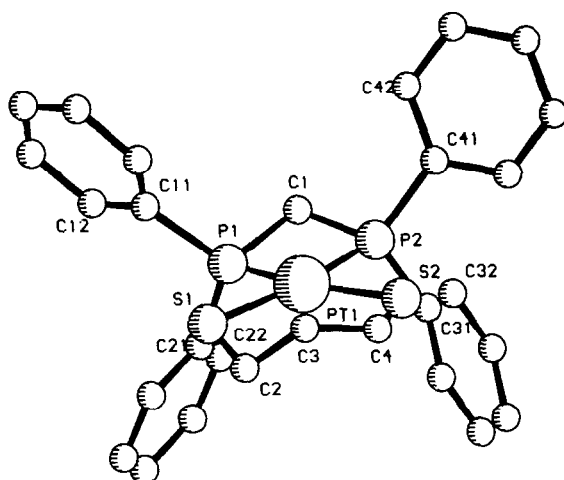
Table

Entry	Thiol	Halide	Solvent	Product	Yield
1	ⁿ BuSH	nBuI	acetone	(ⁿ Bu) ₂ S	80%
2	PhSH	EtBr	acetone	PhSEt	75%
3		EtI *	acetone		92%
4		MeI *	acetone		80%
5	ⁿ PrSH *	CH ₂ I ₂	MeOH	(ⁿ PrS) ₂ CH ₂	66%
6		CH ₂ I ₂	acetone		70%
7		CH ₂ Br ₂	acetone	incomplete	
8		CH ₂ Cl ₂	acetone	no reaction	

* = 2 equiv.

Particularly interesting is the application to thioacetal formation; thiols react successfully not only with monohalides but also with 1,1- dihalides to give thioacetals in good yields (entries 5,6). The intermediate chelated 1,3-dithiolatopropane complex (2) was prepared by treatment of $[\text{PtCl}_2(\text{dppm})]$ with excess dithiol in the presence of sodium carbonate. Complexes (1) and (2) have been characterised by elemental analysis and ^{31}P nmr spectroscopy,³ and a single crystal X-ray structure determination on (2)⁴ confirms its mononuclear chelated structure (Figure).

The complexes neither react with ketones nor catalyse any reaction between thiols and carbonyl groups. This procedure therefore provides a simple and complementary alternative to the more conventional methods of thioacetal formation using thiols and ketones and is especially attractive for thioacetals unsubstituted at the 2 position, preparations of which would normally require the use of formaldehyde or an equivalent or the pre-formation of thiolate anions.



The structure of $\text{Pt}(\text{dppm})(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})$ (2) with H atoms omitted. Selected bond lengths (\AA) and angles ($^\circ$) are: Pt-P(1) 2.236(3), Pt-P(2) 2.276(4), Pt-S(1) 2.332(4), Pt-S(2) 2.276(4), S(1)-C(2) 1.77(2), C(2)-C(3) 1.49(3), C(3)-C(4) 1.42(3), C(4)-S(2) 1.78(3) \AA ; P(1)-Pt-P(2) 72.6(1), P(1)-Pt-S(1), 96.3(1), P(2)-Pt-S(2) 92.7(1), S(1)-Pt-S(2) 98.4(1), P(1)-C(1)-P(2) 92.8(6) $^\circ$.

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2. For other methods of sulphide preparation see, for example: L.M. Harwood, in "General and Synthetic Methods", Vol. 9, R.S.C., London, 1987, pp. 267 - 270; D.N. Harpp, M. Gingras, T. Aida, and T.H. Chan, *Synthesis*, 1987, 1122; K. Takagi, *Chem. Lett.*, 1986, 1379; S. Fujisaki, I. Fujiwara, Y. Norisue, and S. Kajigaeshi, *Bull.Chem.Soc.Japan*, 1985, **58**, 2429; M. Yamato, Y. Takeuchi, K. Hattori, and K. Hashigaki, *Synthesis*, 1982, 1014; G.C. Barrett, in "Comprehensive Organic Chemistry", Vol. 3, Pergamon, Oxford, 1979, pp. 36 - 53.
3. ^{31}P Nmr parameters (in acetone/acetone- d_6 , shifts relative to H_3PO_4) : (1) d(P), -48.1 ppm; J(Pt-P), 2330 Hz; (2) d(P), -50.8 ppm, J(Pt-P), 2274 Hz.
4. Crystal data for (2) : $\text{C}_{28}\text{H}_{28}\text{P}_2\text{PtS}_2 \cdot 0.5 \text{C}_6\text{H}_6$, $M=724.8$, monoclinic, space group $\text{P}2_1/c$, $a=9.318(6)$, $b = 22.76(1)$, $c=15.511(10)$ Å, $\beta=116.52(1)^\circ$, $U=2943.4$ Å 3 , Mo- K_α radiation, $l=0.71069$ Å, $Z = 4$, $D_c=1.63$ g cm $^{-3}$, $D_o= 1.59$ g cm $^{-3}$, $m(\text{Mo-}K_\alpha) = 52.71$ cm $^{-1}$. The structure was solved by Patterson and heavy atom phased Fourier methods (SHELX 5) using 3235 reflections with $F > 4\sigma(F)$ measured on a Stoe Stadi-2 diffractometer. Least squares refinement with anisotropic Pt, S, P, and non-aromatic C atoms converged to $R = 0.049$. All non-aromatic H atoms constrained to ideal methylene geometry, with C-H = 1.08 Å. H atoms on sulphide ligand constrained to $U_{11}=0.08$. Phenyl rings constrained to be regular hexagons with C-C = 1.395 Å. High anisotropic vibration parameters for sulphide carbons thought to be due to some conformational disorder. 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.
5. G.M Sheldrick, "SHELX-76, a program for crystal structure solution and refinement", Cambridge University Press, 1976.

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