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Preliminary communication

A notice: incorrect formulation in the synthetic method of 2,2′-bis(diphenylphosphino)biphenyl

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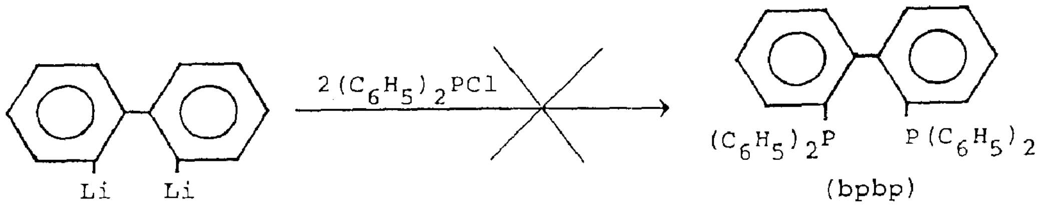
Abstract

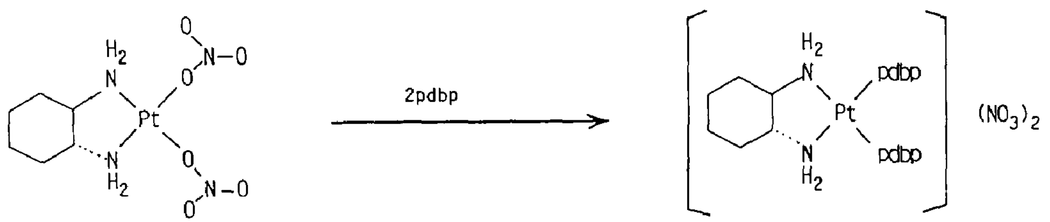
The reaction of 2,2′-dilithiobiphenyl with chlorodiphenylphosphine gives a mixture of triphenylphosphine and 5-phenyldibenzophosphole in almost equal quantities. The formation of the latter phosphine was confirmed by X-ray diffraction study of its platinum(II) derivative. The ^{31}P and ^{13}C NMR data also support the formulation of this reaction. All these experimental facts together clearly demonstrate that the previously reported synthetic method of 2,2′-bis(diphenylphosphino)biphenyl was erroneously formulated.

In the course of our research on chiral recognition by antineoplastic platinum(II) complexes [1,2], we accidentally found that the synthetic method of 2,2′-bis(diphenylphosphino)biphenyl (bpbp), which was reported in this journal [3], is in serious error. In view of the potential usefulness of a prochiral bpbp in the field of organometallic chemistry or of coordination chemistry, we wish to place a notice here.

We attempted to isolate bpbp by exactly the same procedure as described in the literature [3] (Scheme 1). By the reaction of 2,2′-dilithiobiphenyl with chlorodiphenylphosphine, a white solid product was obtained. It had m.p. of 74–85 °C slightly



Scheme 1.



Scheme 2.

different from the reported value (68–70 °C) [3]. Surprisingly enough, its ^{31}P NMR in $CDCl_3$ showed two singlets (δ −8.0 and −12.7, external standard 85% H_3PO_4) with almost equal intensities, indicating that the obtained solid was a mixture of two phosphine species.

The mixture was separated into two species by TLC (silica gel) using n-hexane as the eluent. After separation, each fraction showed one singlet in its ^{31}P NMR ($CDCl_3$) spectrum. The phosphine species with the large R_f value had a chemical shift at −12.7, while the other, with the small R_f value, showed a resonance at −8.0. Thus the latter is assignable to triphenylphosphine (tpp) [4]. Since the former phosphine species could not be identified solely from its NMR spectra, we prepared the platinum(II) derivative of this phosphine ligand and determined its crystal structure.

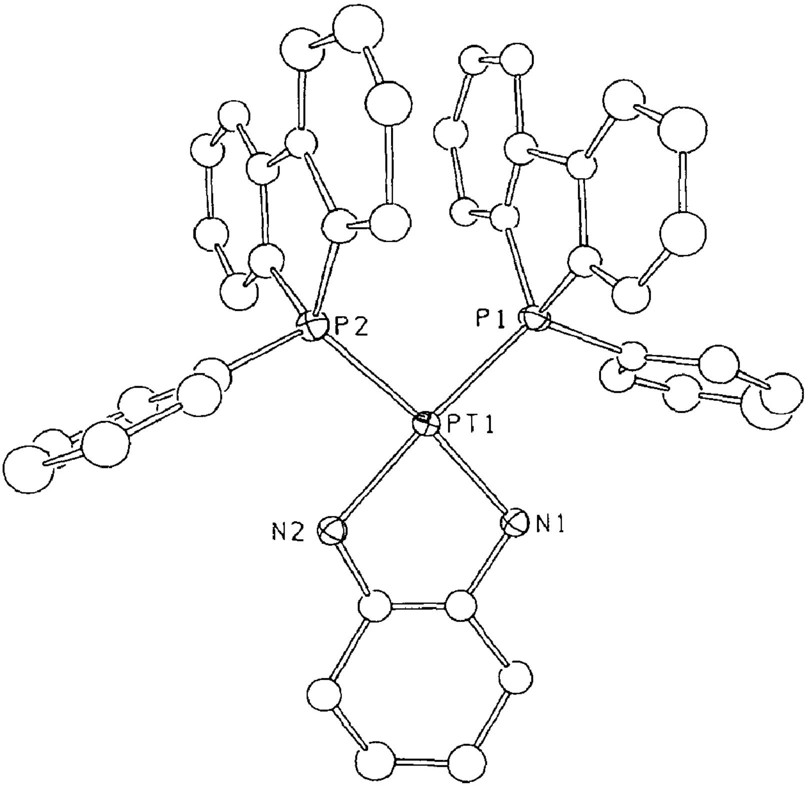


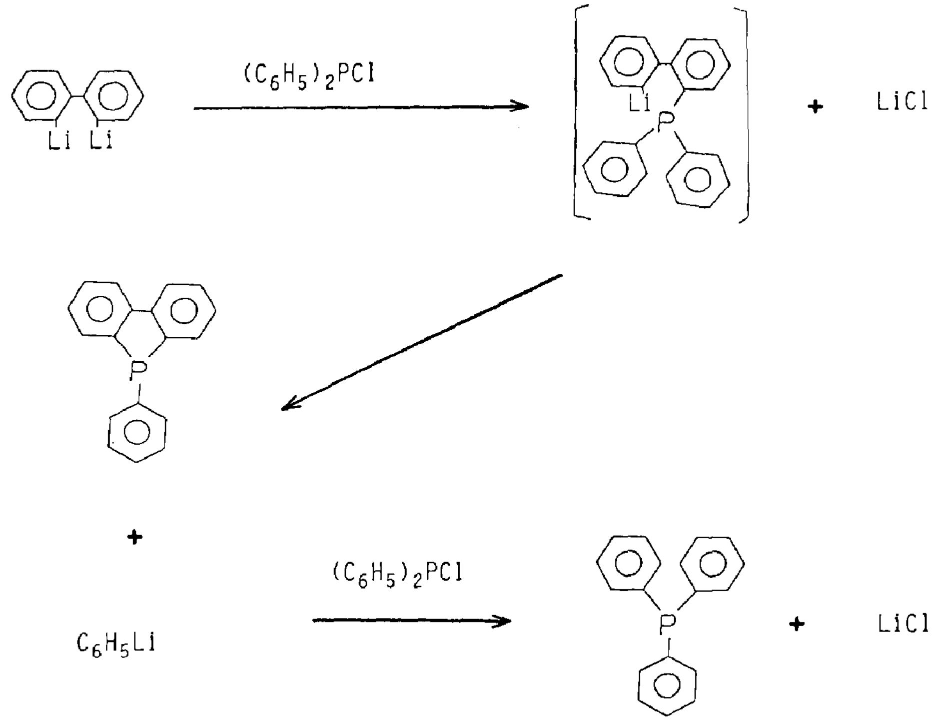
Fig. 1. Molecular structure of the cation, $[Pt(RR\text{-}dach)(pdbp)_2]^{2+}$.

The platinum(II) complex was prepared as follows (Scheme 2). An acetone solution (30 ml) containing the former phosphine species (0.0358 g) was added to an aqueous solution (8 ml) of dinitrato [(1*R*,2*R*)-1,2-diaminocyclohexane]platinum(II), $[Pt(RR\text{-}dach)(NO_3)_2]$ (0.0297 g, 0.0685 mmol). The reaction mixture was concentrated until the precipitation occurred (yield: 0.0554 g). Recrystallization of the crude product from chloroform gave colorless prisms of the dihydrate [*,**].

From the X-ray diffraction study [***], the phosphorus ligand was determined to be 5-phenyldibenzophosphole (pdbp). The molecular structure of $[Pt(RR\text{-}dach)(pdbp)_2]^{2+}$ is illustrated in Fig. 1.

The formulation of the phosphine species as tpp or pdbp was also supported by the ^{13}C or ^{31}P NMR spectrum in complete agreement with those of authentic samples [4,5]. The ^{13}C and ^{31}P NMR data are summarized in Table 1.

The data show that tpp and pdbp instead of bpbp are produced by the procedure described [3]. The formation is proposed in Scheme 3. Several reasons support our suggested mechanism. First, the present experimental conditions [3] are very similar



Scheme 3.

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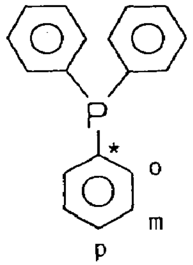
[*] Elemental Analysis Found: C,50.12; H,4.44; N,5.63. $C_{42}H_{44}N_4O_8P_2Pt$ Calcd.: C,50.96; H,4.48; N,5.66%.

[**] $^{31}P\{^1H\}$ NMR($CDCl_3$): δ −8.28 (J(P–Pt)3240). $^{195}Pt\{^1H\}$-NMR($CDCl_3$, external standard 1.2 *M* Na_2PtCl_4 in D_2O): δ −4430(*J*(P–Pt)3220 Hz).

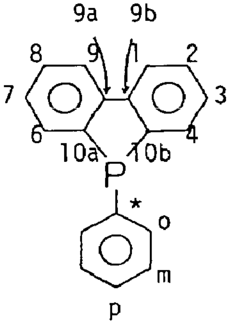
[***] Crystallographic data for $[Pt(R,R\text{-}dach)(PC_{18}H_{13})_2](NO_3)_2 \cdot 2H_2O$: FW = 989.87, triclinic, *P*1, *a* 11.965(2), *b* 17.064(2), *c* 11.304(2) Å, α 101.62(1), β 111.52(1), γ 98.01(1)°, *V* 2045(1)Å^3, $Z = 2$, D_x 1.61, D_m 1.61 g cm^{-3}, $R = 0.041$, w$R = 0.055$ for 10096 independent reflections. Details of the X-ray diffraction study will be published elsewhere.

Table 1

^{31}P and ^{13}C NMR data of two phosphine species



triphenylphosphine
(tpp)



5-phenyldibenzophosphole
(pdbp)

Phosphine	^{31}P NMR	^{13}C NMR		
	δ	δ	J(P–C) (Hz)	Assignment
tpp	−8.01	137.3	11.6	*
		133.8	19.5	*o*
		128.5	6.7	*m*
		128.6		*p*
pdbp	−12.72	142.6		10a,b
		143.6		9a,b
		128.8		1
		121.4		2
		127.6	7.3	3
		130.4	21.4	4
		133.8	19.5	*
		132.7	20.1	*o*
		128.6	7.9	*m*
		129.2		*p*

to those of the established synthetic method of pdbp [5]. Second, approximately equal amounts of two phosphine species, tpp and pdbp, were actually detected in the ^{31}P NMR spectrum of the original mixture in the present work.

Recently, bpbp was prepared in an alternative way by a gold(I) complex [7]. The white crystalline product, bpbp, melts at a high temperature (212° C) and its ^{31}P NMR spectrum shows a singlet at -15.0 (CD_2Cl_2). Judging from these reported values, the published method [3] is again not reliable or erroneous for the preparation of bpbp. For the practical preparation of large amounts of bpbp a different methodology is obviously required.

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