

Synthesis and a Crystal Structure Analysis of Mixed Bis(phosphino)methanide/Phosponium Bis(methylide) Complexes of Nickel, Palladium, and Platinum

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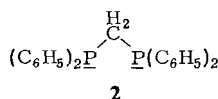
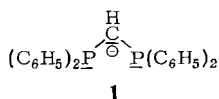
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From bis(diphenylphosphino)methanide complexes of the type $\{[(C_6H_5)_2P]_2CH_2\}_2M$ ($M = Ni, Pd, Pt$), and an equivalent amount of an ylide $R_2(CH_3)P=CH_2$ ($R = CH_3, C_2H_5$), the three title complexes $\{[(C_6H_5)_2P]_2CH\}M[(CH_2)_2PR_2]$ (**5a–c**) have been prepared. $CH_2[P(C_6H_5)_2]_2$ is the by-product of the reaction. An X-ray diffraction study of the platinum compound **5c** revealed a mixed chelate structure with a planar bis(phosphino)methanide and a folded ylide ring. The central carbon of the bis(phosphino)methanide is not in close contact with the metal. Its distances to the phosphorus atoms indicate significant double bond character, some of which is also retained in the phosponium bis(methylide) group.

Synthese und eine Kristallstrukturanalyse von gemischten Bis(phosphino)methanid/Phosponium-bis(methylid)-Komplexen des Nickels, Palladiums und Platins

Aus den Bis(diphenylphosphino)methanid-Komplexen des Typs $\{[(C_6H_5)_2P]_2CH_2\}_2M$ ($M = Ni, Pd, Pt$) und der äquivalenten Menge eines Ylids $R_2(CH_3)P=CH_2$ ($R = CH_3, C_2H_5$) wurden die drei Titelverbindungen $\{[(C_6H_5)_2P]_2CH\}M[(CH_2)_2PR_2]$ (**5a–c**) erhalten. Eine Röntgenbeugungsanalyse der Platinverbindung **5c** ergab eine gemischte Chelatstruktur mit einem ebenen Bis(phosphino)methanid- und einem gefalteten Ylidring. Das mittlere C-Atom des Bis(phosphino)methanids unterhält keine direkten Kontakte zum Metall. Seine Abstände zu den P-Atomen deuten erheblichen Doppelbindungscharakter an. Ylidischer Doppelbindungscharakter wird auch in der Phosponium-bis(methylid)-Gruppe beibehalten.

It is more than ten years since *Issleib* and coworkers first showed that the bis(diphenylphosphino)methanide anion **1** with its carbanionic centre between two phosphane donors is a very strong ligand to transition metals. Such complexes, however, were difficult to characterize due to their low solubility¹, and with very few exceptions, this important result has not been exploited any further^{2,3}. It was only in the case of the copper(I) derivative that the solid state structure could be determined by X-ray diffraction². The ligands in this complex, shown to be a trimer, were found to be bridging two- and three-coordinate copper atoms such that both phosphorus atoms and the central carbanion were involved in coordinative bonding.



molecular weights. The *NMR spectra* also give no evidence for association to dimers or oligomers and can be readily interpreted by the monomeric formulae. The ^1H , ^{13}C , and ^{31}P NMR data are summarized in table 1. The $^{31}\text{P}\{^1\text{H}\}$ resonances are clearly separated doublet/triplet signals of the expected ratio 2:1 for the phosphorus atoms in **1** and $\text{R}_2\text{P}(\text{CH}_2)_2^\ominus$, respectively. In the case of **5c**, they are accompanied by the expected ^{195}Pt - ^{31}P satellite signals.

Table 1. NMR Spectra of Complexes **5a–c**

	Ni	Pd	Pt
^1H Solvent	$[\text{D}_8]\text{Toluene}$	$[\text{D}_8]\text{Toluene}$	$[\text{D}_6]\text{Benzene}$
δCH_2	-0.45, dt	-0.35, m	a)
$^2J(\text{PH}), ^3J(\text{PH})$	6.2; 1.7	5.0; 2.2	
δR	0.98, d	0.83/0.47, m	0.98, d
$^2J(\text{PH})$	12.5	$\text{A}_3\text{B}_2\text{X}$	12.4
δCH	2.65, t	2.90, t	2.23, t
$^2J(\text{PH})$	3.1	3.0	4.8
^{13}C δCH_2	-16.4, m	-	a)
spin system	$\text{A}'\text{XX}'\text{Y}$	-	
δCH_3	22.7, d	-	a)
$^1J(\text{PC})$	34.0	-	
δCH	23.8, t	-	a)
$^1J(\text{PC})$	51.0	-	a)
^{31}P Solvent	$[\text{D}_6]\text{Benzene}$	$[\text{D}_8]\text{Toluene}$	$\text{C}_6\text{H}_5\text{Cl}, \text{C}_6\text{D}_6$
δP_A	-25.55, s	-25.3, d	-44.3, d
δP_B	9.88, s	21.2, t	28.1, t
$^3J(\text{PP})$	-	8.0	15.0
$^1J(\text{PtP}), ^2J(\text{PtP})$	-	-	2072; 555

a) Poor solubility in suitable solvents prevented identification of these resonances.

One such coupling constant ($^1J(\text{PtP}) = 2072$ Hz) is significantly greater than that found for the complex *cis*- $\{\text{CH}_2[\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Pt}(\text{C}_6\text{H}_5)_2\}^{\text{9)}$. Rather than concluding that this is due to a shortening, by 0.02 Å, of the Pt–P bonding distance (see below), it is more reasonable to suggest that it is a reflection of an increased *s* character at the phosphorus in the ligand **1** as compared to **2**. ^1H - and ^{13}C spectra are characterized by more complex spin systems, but those can be easily assigned by their chemical shifts and relative intensities.

The *IR spectra* show no unexpected features.

Crystal Structure of the Platinum Compound **5c**

The procedure for the structure determination and the refinement are described in the experimental section below, the results are summarized in figures 1, 2 and table 2.

The molecule has crystallographically imposed C_s symmetry, with the metal atom Pt, the ylide phosphorus P(2), and the carbanion C(1) of the bis(phosphino)methanide

lying in the mirror plane with the methyl carbons C(21) and C(22). Perpendicular to the mirror plane is the plane of coordination, approximately square, around the platinum atom. Significant distortions away from an ideal square planar arrangement of ligand atoms P(1), P(1'), C(2), and C(2)' are apparently due to the small bite of the chelating ligands, as illustrated by the angles P(1)–Pt–P(1)' = 69.6°, and C(2)–Pt–C(2)' = 73.9°.

Table 2. Intramolecular distances (Å) and bond angles (°) as well as final positional (fractional coordinate) and thermal parameters for the platinum complex **5c**, Pt[(CH₂)₂PMe₂][(PPh₂)₂CH], with estimated standard deviations in parentheses

				Atom	X	Y	Z	Population			
Pt – P(1)	2.276(5)	P(1) – Pt – P(1)'	69.6(2)	Pt	0.3718(6)	0.06399(6)	0.0	0.5			
Pt – C(1)	3.050(19)	C(2) – Pt – C(2)'	73.9(7)	P(1)	0.35073(28)	0.17158(31)	0.06286(22)	–			
Pt – C(2)	2.185(19)	P(1) – C(1) – P(1)'	95(1)	P(2)	0.36297(47)	0.09610(41)	0.0	0.5			
Pt – P(2)	2.733(7)	C(2) – P(2) – C(2)'	99.3(9)	C(1)	0.3426(16)	0.2404(15)	0.0	0.5			
P(1) – C(1)	1.756(17)	C(21) – P(2) – C(22)	105(1)	C(2)	0.3907(11)	–0.0367(11)	0.0635(9)	–			
P(1) – C(301)	1.85(2)	C(21) – P(2) – Pt	104.0(6)	C(21)	0.2570(14)	–0.1164(13)	0.0	0.5			
P(1) – C(401)	1.03(2)	C(22) – P(2) – Pt	151(1)	C(22)	0.4092(22)	–0.1907(26)	0.0	0.5			
		C(21) – P(2) – C(2)	112.3(9)	C(301)	0.4261(15)	0.1959(12)	0.1244(10)	–			
C(2) – P(2)	1.724(19)	C(22) – P(2) – C(2)	114(1)	C(302)	0.4697(15)	0.2722(14)	0.1197(14)	–			
P(2) – C(21)	1.84(2)	Pt – C(2) – P(2)	87.9(8)	C(303)	0.5279(16)	0.2851(17)	0.1731(16)	–			
P(2) – C(22)	1.80(4)	Pt – P(1) – C(1)	97.4(7)	C(304)	0.5412(22)	0.2200(21)	0.2151(15)	–			
C(301) – C(302)	1.50(3)	C(301) – P(1) – C(401)	98.3(9)	C(305)	0.4917(20)	0.1981(18)	0.2200(13)	–			
C(302) – C(303)	1.50(4)	C(301) – P(1) – C(1)	114(1)	C(306)	0.4444(11)	0.1404(13)	0.1685(11)	–			
C(303) – C(304)	1.44(5)	C(301) – P(1) – Pt	117.5(7)	C(401)	0.2644(11)	0.1734(11)	0.1151(8)	–			
C(304) – C(305)	1.36(5)	C(401) – P(1) – C(1)	110.5(9)	C(402)	0.2483(11)	0.2322(7)	0.1535(9)	–			
C(305) – C(306)	1.37(4)	C(401) – P(1) – Pt	119.6(6)	C(403)	0.1748(13)	0.2333(13)	0.1689(11)	–			
C(306) – C(301)	1.35(3)	C(301) – C(302) – C(303)	114(2)	C(404)	0.1319(14)	0.1742(14)	0.1827(12)	–			
C(401) – C(402)	1.28(3)	C(302) – C(303) – C(304)	115(3)	C(405)	0.1428(14)	0.1369(14)	0.1399(11)	–			
C(402) – C(403)	1.45(3)	C(303) – C(304) – C(305)	124(3)	C(406)	0.2140(13)	0.1152(13)	0.1095(12)	–			
C(403) – C(404)	1.25(3)	C(304) – C(305) – C(306)	119(3)	ii(211) [†]	0.2295	–0.0633	0.0	10 ² U ₃₃ 7.1			
C(404) – C(405)	1.34(3)	C(305) – C(306) – C(301)	120(2)	Thermal parameters (Å ² × 10 ³) for non-hydrogen atoms with estimated standard deviations in parentheses.							
C(405) – C(406)	1.37(3)	C(306) – C(301) – C(302)	122(2)	Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	
C(406) – C(401)	1.34(3)	C(401) – C(402) – C(403)	120(2)	Pt	2.84(6)	2.52(6)	1.98(3)	0.10(5)	0.0	0.0	
		C(402) – C(403) – C(404)	117(2)	P(1)'	3.6(2)	2.9(2)	2.1(1)	–0.3(2)	0.1(1)	–0.3(1)	
		C(403) – C(404) – C(405)	124(2)	P(2)'	1.1(3)	4.7(4)	3.8(3)	–1.3(3)	0.0	0.0	
		C(404) – C(405) – C(406)	116(2)	C(1)'	5(1)	2(1)	4(1)	2(1)	0.0	0.0	
		C(405) – C(406) – C(401)	121(2)	C(2)'	6(1)	1.8(8)	2.8(7)	1.6(8)	–0.4(6)	0.1(6)	
		C(406) – C(401) – C(402)	124(1)	C(21)'	0.5(9)	4(1)	3(1)	–0.4(8)	0.0	0.0	
				C(22)'	4(2)	8(2)	8(2)	–6(2)	0.0	0.0	
				C(301)	3.6(3)						
				C(302)	5.3(5)						
				C(303)	6.5(6)						
				C(304)	7.2(7)						
				C(305)	6.7(6)						
				C(306)	3.9(4)						
				C(401)	2.9(3)						
				C(402)	3.1(3)						
				C(403)	4.3(4)						
				C(404)	4.5(4)						
				C(405)	4.5(4)						
				C(406)	3.9(4)						
Calculated Positions of Hydrogen Atoms											
	X	Y	Z	10 ³ U _{eq} ²							
H(212)	0.2423	–0.1461	0.0395	7.1							
H(1')	0.4489	–C.0443	0.0788	6.3							
H(2)	0.3531	–0.0390	0.1038	6.3							
H(302)	0.4520	0.3148	0.0915	7.1							
H(303)	0.5539	0.3332	0.1790	7.1							
H(304)	0.5790	0.225 ^o	0.2667	7.1							
H(305)	0.5128	0.1212	0.2512	7.1							
H(306)	0.4168	0.0872	0.1705	7.1							
H(402)	0.2829	0.2777	0.1517	7.1							
H(403)	0.1614	0.2818	0.2117	7.1							
H(404)	0.0765	0.1724	0.2075	7.1							
H(405)	0.1035	0.0721	0.1372	7.1							
H(406)	0.2264	0.0695	0.0830	7.1							

^o Atom related by symmetry operation X, Y, Z.

[†]Anisotropic temperature factors in the form $\exp[-z^2r^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k^2b^*c^*)]$.

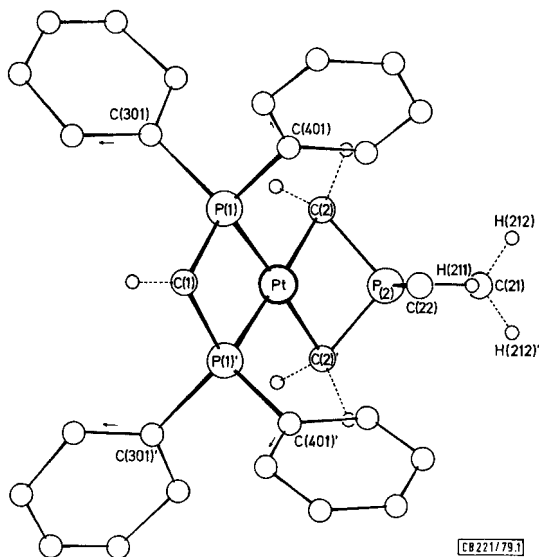


Fig. 1. Molecular structure of the platinum complex **5c** and atomic numbering (bond lengths and bond angles see table 2 and text)

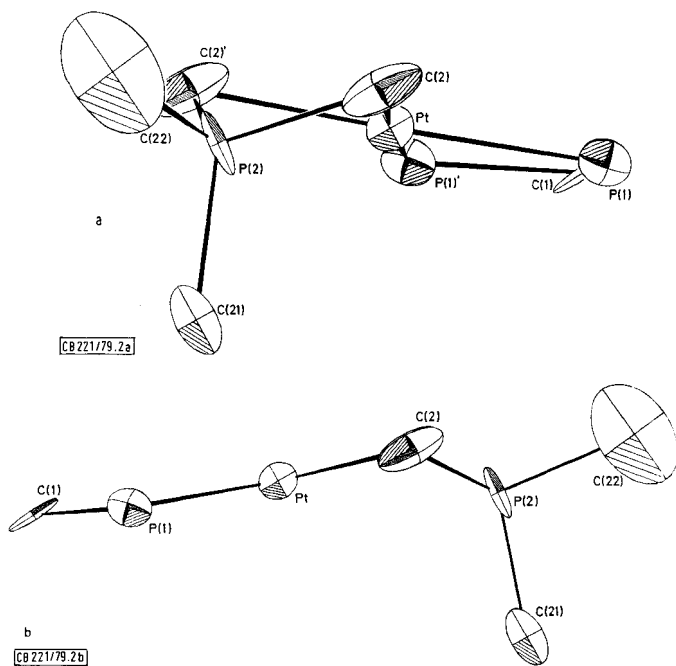
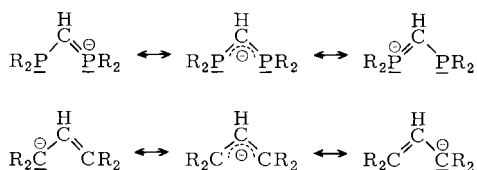


Fig. 2. Two different projections of the heavy atom skeleton in the platinum complex **5c**, showing the folding of the ylide ring and the planarity of the bis(phosphino)methanide ring

As shown in figures 2a) and 2b) the chelate ring of the ylide is folded by ca. 40° along the line drawn across the ring through C(2) and C(2'). This folding is typical for ylide complexes and was also found in an analogous nickel compound⁷⁾. In solution the ring appears to be sufficiently flexible to render the two CH₃ (**5a, e**) and C₂H₅ groups (**5b**) equivalent on the NMR time scale, through ring inversion. It should be pointed out, however, that in an octahedral ylide complex of cobalt(III) the CoCPC chelate ring is nearly planar, possibly imposed by a steric effect, which is absent in square planar systems⁷⁾. Bond lengths of the ylide chelate are not unusual, in that according to the distances P(2)–C(2) and P(2)–C(2') of 1.72(2) Å the ylide C(2)–P(2)–C(2') has still retained some double bond character.

The P(1)–C(1) distance of 1.76(2) Å is shorter by 0.1 Å than that established for the neutral ligand **2** in the complex *cis*-[CH₂[P(C₆H₅)₂]₂Pt(C₆H₅)₂]⁹⁾, suggesting significant double bond character, which together with the near coplanarity of atoms Pt, P(1), P(1'), and C(1) (within ±0.02 Å) confirms the formulation of this ligand as the bis(diphenylphosphino)methanide anion Ph₂P=C=CH=PPh₂[⊖] (**1**). While the latter has been shown to exist in a bridging role in the copper complex²⁾, our platinum complex represents the first structurally characterized example containing **1** as a chelating ligand.

Although originally considered analogous, in a valence bond description¹⁾, to an η³-allyl function, in the light of structural evidence presented here, the bonding of **1** with a metal is clearly different.



While the ligated P atoms P(1) and P(1') lie about 2.28 Å from the platinum, the Pt–C(1) distance of 3.05(2) Å is not to be considered a bonding interaction.

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Experimental Part

All experiments have been carried out under an atmosphere of dry oxygen-free nitrogen and in carefully purified and dried solvents saturated with nitrogen. Glass apparatus was treated accordingly. – NMR spectra: spectrometers Jeol C-60 HL, Jeol FX 60, and Bruker HFX 90.

Nickel(II) [bis(diphenylphosphino)methanide] [dimethylphosphonium bis(methylide)] (5a): To a stirred suspension of [CH[P(C₆H₅)₂]₂]₂Ni (**4a**) (1.84 g, 2.2 mmol) in 20 ml benzene is added (CH₃)₃PCH₂ (0.20 g, 2.2 mmol). After 15 min the resulting clear solution is filtered, concentrated in vacuo to ca. 7 ml, and pentane is added before cooling to –20°C to precipitate the product (0.76 g, 53% yield) as yellow crystals decomposing at 90°C.

C₂₉H₃₁NiP₃ (531.2) Found C 65.60 H 5.81 Calc. C 65.57 H 5.88

Palladium(II) [bis(diphenylphosphino)methanide] [diethylphosphonium bis(methylide)] (5b): A suspension of Pd[CH[P(C₆H₅)₂]₂]₂ (**4b**) (2.18 g, 2.5 mmol)¹) in benzene is treated with CH₃(C₂H₅)₂PCH₂ (0.28 g, 2.5 mmol). The resulting yellow solution is concentrated in vacuo and the residue dissolved in 5 ml of toluene. On careful addition of an upper layer of pentane pale yellow crystals separate (0.74 g, 75% yield). With more pentane and on cooling CH₂[P(C₆H₅)₂]₂ is also precipitated. **5b**: m.p. 150 °C.

C₃₁H₃₅P₃Pd (607.9) Found C 61.35 H 5.83 Calc. C 61.25 H 5.97

Platinum(II) [bis(diphenylphosphino)methanide] [dimethylphosphonium bis(methylide)] (5c): In a procedure similar to that described for **5a**, 2.1 g of [CH[P(C₆H₅)₂]₂]₂Pt (**4c**) and 0.2 g of (CH₃)₃PCH₂ (2.2 mmol each) were reacted in 30 ml of toluene; 1.0 g yield (68%). Pale yellow crystals (from toluene/pentane), m. p. 155 °C (decomp.).

C₂₉H₃₁P₃Pt (667.6) Found C 52.30 H 5.30 Calc. C 52.17 H 4.68 Molecular Mass 667(MS)

Crystal Data: C₂₉H₃₁P₃Pt, M = 667.6. Tetragonal space group *I* 4/*m*, *a* = 17.047 (8), *b* = 17.048 (8), *c* = 20.667 (9) Å. *V* = 6006.1 Å³, *Z* = 8, *D_m* = 1.49 g cm⁻³, *F*(000) = 2624; Mo-*K*_α radiation, graphite monochromator, λ = 0.71069 Å; μ(Mo-*K*_α) = 50.9 cm⁻¹. Syntex P2₁ diffractometer, room temperature.

Solution of the Structure: The compound forms pale yellow tetragonal prisms. One such crystal, chosen for its clean appearance and transparency, and of approximate dimensions 0.4 × 0.25 × 0.25 mm, was mounted on a glass fibre with epoxy resin adhesive.

Precession photographs revealed 4/*m* symmetry and the observed systematic absences (*hkl*, *h* + *k* + *l* = 2*n* + 1) defined the space group *I* 4/*m* for a tetragonal cell having the above dimensions. As density measurements suggested the existence of 8 formula units per unit cell, and no further systematic absences other than those required by the space group were identified, it was deduced that the molecule was bisected by the mirror plane (001).

Preliminary diffractometer experiments confirmed the choice of unit cell and space group assignments. Of 1543 measured intensities (ω scan, 0° < 2θ ≤ 50°), 1097 were deemed observed by the criterion *I* > 1.96 σ(*I*), where σ is the estimated standard deviation of the intensity based on counter statistics.

A Patterson synthesis and MULTAN were used to locate the platinum and the two independent phosphorus atoms. Corrections for anomalous dispersion to the scattering factors of Pt and also for absorption were applied, while full matrix least squares refinement of the atomic positions and difference Fourier syntheses provided the remaining non-hydrogen atoms. Refinement of these and a difference Fourier using only those data for which sin θ · λ⁻¹ ≤ 0.34 led to the location of hydrogen atom H(211), from which the other bonded to methyl carbon C(21) was calculated (the third being related by the symmetry operation *X*, *Y*, \bar{Z}). Phenyl hydrogens were introduced at calculated positions. While all hydrogen atom parameters were held invariant and phenyl carbon atoms were refined with isotropic temperature factors only, all others were allowed anisotropic thermal parameters. Full matrix least squares refinement using only those data (1049) for which *F* ≥ 40.0 and the weighting scheme $W^{-1} = \sigma^2(F) + (0.01 F_0)^2$, but excluding four strong low angle reflections judged to be suffering from secondary extinction, led to convergence at *R* = 0.055 (*R*' = 0.059). A final electron density difference synthesis revealed no residuals greater than 0.4 e Å⁻³.

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