Reactions of Some Tertiary Phosphines with (But-3-enyl n-butyl sulphide)dichloropalladium(II)

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The reaction of PPh_3 with $[Pd(bbs)Cl_2]$ (1 : 1), where bbs is but-3-enyl n-butyl sulphide, gives the unusual bridged palladium(II) complex $[Cl_2(Ph_3P)Pd(\mu\text{-bbs})Pd(PPh_3)Cl_2]$, which has been characterised by elemental analysis and *X*-ray photoelectron and vibrational spectroscopy. Triethylphosphine behaves differently, giving a mixture of two complexes, $[Pd(PEt_3)_2Cl_2]$ and *trans*-$[Pd(bbs)_2Cl_2]$, the latter containing unidentate bbs co-ordinated *via* sulphur only. Confirmation of the structure of *trans*-$[Pd(bbs)_2Cl_2]$ has been obtained by preparing the complex both from palladium(II) chloride and bbs (1 : 2), and from $[Pd(bbs)Cl_2]$ and bbs (1 : 1). All attempts to prepare *cis*-$[Pd(PPh_3)_2Cl_2]$ by displacement of a chelating ligand from either a *cis*-dichloro or a *cis*-bis(triphenylphosphine) complex, including repetition of literature methods reported to yield this product, have led to the formation of *trans*-$[Pd(PPh_3)_2Cl_2]$, together with the bridged complex in the case of $[Pb(bbs)Cl_2]$.

As part of an investigation into the action of strong acids on low-valent transition-metal complexes,[1] we wished to prepare the complex *cis*-$[Pd(PPh_3)_2Cl_2]$. The analogous platinum(II) complex may be readily obtained,[1,2] but standard preparative routes lead invariably to the *trans* palladium isomer.[2,3] Nevertheless the desired complex has been reported several times in the literature.[4-10] A closer examination reveals a surprising lack of information, however. Druding and Shupack [4] mentioned *cis*-$[Pd(PPh_3)_2Cl_2]$ as being prepared by standard methods,[11] but no physical criteria for the stereochemistry were given, and the product was almost certainly the *trans* isomer. Goodall [5] reported the isolation of *cis*-$[Pd(PPh_3)_2Cl_2]$ as yellow crystals from the reaction of PPh_3 (2 mol) and $[PdCl_2(bbs)]$ (1 mol) in methanol, where bbs is but-3-enyl n-butyl sulphide. The structure was supported by elemental analysis (C, H, and Pd) and i.r. spectroscopy, which showed the expected two Pd–Cl stretching frequencies at 327 and 300 cm^{-1}. Marbach and Pascal claimed [6] to have made the *cis* complex by the method of Itatani and Bailar,[12] but this preparation undoubtedly yields the *trans* complex.

The fourth apparent reference to *cis*-$[Pd(PPh_3)_2Cl_2]$ is due to an indexing error.[13] The original article reported that reaction of the chelated complex $[Pd(O_2C_6Cl_4)(PPh_3)_2]$ with HCl gas gave a 94% yield of *trans*-$[Pd(PPh_3)_2Cl_2]$. The corresponding platinum(II) complex gave a 96% yield of *cis*-$[Pt(PPh_3)_2Cl_2]$,[7] showing the difference in stabilities of the *cis* complexes of these metals. More recently, three separate groups of workers have mentioned *cis*-$[Pd(PPh_3)_2Cl_2]$ as a starting material,[8-10] without giving details of its preparation or properties.

The only source of physical data for the required complex thus appears to be the paper by Goodall,[5] but even this preparation is surprising in view of the apparent instability of *cis*-$[Pd(PPh_3)_2Cl_2]$. We have reinvestigated this reaction, and have isolated small amounts of the unusual yellow bridged complex $[Cl_2(Ph_3P)Pd(\mu\text{-bbs})Pd(PPh_3)Cl_2]$ which has been characterised by analysis and photoelectron and vibrational spectroscopy, together with *trans*-$[Pd(PPh_3)_2Cl_2]$. Larger quantities of the bridged species were obtained from the reaction of equimolar quantities of $[Pd(bbs)Cl_2]$ and triphenylphosphine. No evidence for the formation of *cis*-$[Pd(PPh_3)_2Cl_2]$ was found, either from this or related reactions.

Triethylphosphine reacts with $[Pd(bbs)Cl_2]$ (1 : 1) to give a mixture of $[Pd(PEt_3)_2Cl_2]$ and the new complex *trans*-$[Pd(bbs)_2Cl_2]$ a non-crystallisable oil which contains unidentate bbs co-ordinated through sulphur only. Its structure has been confirmed by elemental analysis, i.r. spectroscopy, and by preparing the complex by alternative routes.

EXPERIMENTAL

Chemicals of the best available commercial grade were used, in general without further purification except for triphenylphosphine which was recrystallised from acetone. But-3-enyl n-butyl sulphide (bbs), 1,2-bis(but-3-enylthio)-ethane (bte), and the complexes $[Pd(bbs)Cl_2]$ and $[Pd(bte)Cl_2]$ were prepared by the procedures given by Goodall.[5] The complex $[Pb(nbd)Cl_2]$ (nbd = norbornadiene) was prepared from $[Pd(NCPh)_2Cl_2]$,[14] kindly donated by Dr. M. J. Harriss. The complex *trans*-$[Pd(PPh_3)_2Cl_2]$ was obtained from palladium(II) chloride and triphenylphosphine by the method of Itatani and Bailar.[12] The complex may be readily identified by analysis and the single strong Pd–Cl stretching vibration in its i.r. spectrum (Nujol mull) close to 360 cm^{-1}.[3]

Carbon and hydrogen microanalyses were obtained by combustion using a Perkin-Elmer 240 elemental analyser. Phosphorus was determined colorimetrically as the complex molybdovanadophosphate after decomposition of the compound by heating with sodium peroxide in a nickel Parr bomb. Chlorine was determined potentiometrically by means of silver nitrate in an aqueous acetone medium. Palladium was analysed spectroscopically on a Perkin-Elmer 403 atomic-absorption spectrophotometer. Sulphur was determined, after combustion in an oxygen flask, by titration against barium perchlorate in aqueous acetone.

Photoelectron spectra were obtained on an A.E.I.-ES200B electron spectrometer using Mg-$K_{\alpha 1,2}$ radiation, the photon energy of which is 1 253.6 eV.* The samples were examined at ambient temperature as powders pressed on to double-sided Scotch tape and mounted on the tip of the sample probe. The pressure in the spectrometer source at the sample position was typically between 10^{-8} and 5×10^{-8} Torr. The *X*-ray flux absorbed in the outermost 100 Å of material, which is the depth examined in *X*-ray photoelectron spectroscopic experiments, was rather less than 100

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* Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J; 1 Torr = (101 325/760) Pa; 1 rad = 10^{-2} J kg^{-1}.

rad h^{-1}. No sign of decomposition was noted for any of the samples, even after a time significantly longer than that required to obtain a spectrum. The binding energies of the various core electrons studied were measured relative to the C 1*s* photoelectron line at 285.0 eV, arising from alkyl or aryl groups on polyatomic ligands in the compounds.[15] Unresolved peaks were deconvoluted on a du Pont 310 curve resolver on the assumption of Gaussian lineshapes. The analogue integrator in the curve resolver was used to measure the relative intensities of the photoelectron lines arising from the core levels of the various elements present, with a reproducibility of better than $\pm 5\%$.

Infrared spectra in the range 250—4 000 cm^{-1} were recorded from Nujol mulls on a Perkin-Elmer 457 spectrometer, using caesium iodide plates covered with Polythene discs to eliminate any possibility of halogen exchange. Raman spectra of the solid samples were recorded on a Cary model 82 laser Raman spectrometer, using the standard powder-sampling device. The 514.5-nm exciting line was provided by a Spectra Physics model 164 argon-ion laser.

Reaction of Triphenylphosphine with [Pd(bbs)Cl$_2$].—A suspension of [Pd(bbs)Cl$_2$] in methanol was heated under reflux for 30 min with triphenylphosphine in a 1 : 2 mol ratio.[5] The mixture was filtered while hot, and a considerable quantity of solid isolated, characterised as *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] by elemental analysis and its Pd–Cl i.r. stretching vibration (Nujol mull) at *ca.* 360 cm^{-1}.[3] Some yellow crystals which appeared when the filtrate was allowed to cool showed two Pd–Cl i.r. stretching absorptions at 329 and 308 cm^{-1}, as expected for a *cis*-dichloro-complex, but did not analyse as [Pd(PPh$_3$)$_2$Cl$_2$] (Table 1). In particular, the Pd : Cl : P ratio appeared to be 1 : 2 : 1 rather than 1 : 2 : 2. Similar results were obtained when the quantity of solvent or the refluxing time were varied. Indeed, stirring of the reagents in methanol for 15 min at room temperature gave a high yield of *trans*-[Pd(PPh$_3$)$_2$Cl$_2$], but no *cis* complexes. Attempts to convert *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] into the *cis* isomer by refluxing in methanol led to recovery of unchanged starting material.

TABLE 1

Comparison of theoretical and observed elemental analyses

	Required (%)				
Complex	C	H	P	Cl	Pd
[Pd(PPh$_3$)$_2$Cl$_2$]	61.6	4.30	8.85	10.1	15.15
[Pd(PPh$_3$)(bbs)Cl$_2$]	53.5	5.35	5.30	12.15	18.2
[Pd(PPh$_3$)Cl$_2$]·MeOH	48.4	4.05	6.55	15.05	22.55
[Pd$_2$(PPh$_3$)$_2$(bbs)Cl$_4$]	51.65	4.55	6.05	13.85	20.8
Found for yellow product	51.1	4.45	6.25	14.05	20.45

The yellow complex was obtained in higher yield by refluxing a 1 : 1 mol ratio of the reagents in methanol. The mixture was filtered while hot, to remove some brown material containing yellow streaks, clearly an inhomogeneous mixture of palladium complexes which was not further investigated. The solid yellow complex separated on cooling, and more was recovered by evaporation of the solvent. The product was identical in its i.r. spectrum and analysis to that from the 2 : 1 reaction (Table 1). No solvent could be found in which the complex was sufficiently soluble for either ^{1}H or ^{31}P Fourier-transform n.m.r. spectra to be obtained.

Reaction of Triethylphosphine with [Pd(bbs)Cl$_2$].—A 1 : 1 mixture of the reagents was stirred for *ca.* 90 min in methanol, and the solvent then removed. Initial reactions gave a deep orange liquid which did not solidify on cooling, but at the third attempt a pale brown solid in an orange-red liquid was obtained. The components were separated and examined; the solid analysed approximately as Pd(PEt$_3$)$_2$Cl$_2$ (Found: C, 32.8; H, 6.65; Cl, 18.0; P, 14.05; Pd, 26.95. $C_{12}H_{30}Cl_2P_2Pd$ requires C, 34.85; H, 7.30; Cl, 17.15; P, 15.03; Pd, 25.7%).

Analysis of the red liquid showed that it, too, was impure, but it appeared to consist mainly of the new complex [Pd(bbs)$_2$Cl$_2$] with bbs acting as a unidentate ligand (Found: C, 40.9; H, 7.10; Cl, 17.05; P, 3.30; Pd, 20.35; S, 9.50. $C_{16}H_{32}Cl_2PdS_2$ requires C, 41.25; H, 6.90; Cl, 15.2; P, 0; Pd, 22.85; S, 13.75%). In order to verify this conclusion, alternative syntheses of [Pd(bbs)$_2$Cl$_2$] were carried out. First, palladium(II) chloride dissolved in 50% aqueous ethanol containing a little HCl was heated under reflux for 4 h with twice the molar quantity of bbs dissolved in ethanol. After removal of solvent a red liquid remained, analysis of which suggested that impurities were present (Found: C, 38.8; H, 6.30; Cl, 12.45; Pd, 20.45; S, 15.45%). A purer product was obtained from equimolar quantities of [Pd(bbs)Cl$_2$] and bbs in methanol. The mixture turned orange-red within minutes, but stirring was continued for 1 h to ensure complete reaction. The methanol was removed to leave an orange-red sticky liquid which did not crystallise, but gave excellent analyses for [Pd(bbs)$_2$Cl$_2$] (Found: C, 41.0; H, 6.50; Cl, 15.1; Pd, 22.55; S, 13.75%).

Reaction of Triphenylphosphine with [Pd(nbd)Cl$_2$].—The palladium complex was dissolved in glacial acetic acid,[14] and twice the equimolar amount of PPh$_3$ added. The mixture was stirred and a yellow precipitate quickly formed. This was isolated, and identified as *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] by elemental analysis and the characteristic Pd–Cl stretching vibration in its i.r. spectrum.[3]

RESULTS AND DISCUSSION

Reaction of Triphenylphosphine with [Pd(bbs)Cl$_2$].—The analytical data given in Table 1 clearly suggest the presence of Pd(PPh$_3$)Cl$_2$ units in the yellow complex, together with other organic residues. The only possibilities for these would seem to be bbs, methanol, or decomposition products thereof. Methanol is an unlikely ligand in view of the recovery of *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] unchanged from this solvent, but the results are such that only one bbs appeared to be combined with two Pd(PPh$_3$)Cl$_2$ units. The complex was therefore investigated by other physical techniques to confirm this hypothesis. The i.r. absorption ascribed to the olefinic double bond in bbs appears at 1 635vs cm^{-1} and at 1 529 cm^{-1} in [Pd(bbs)Cl$_2$],[5] showing the effect of co-ordination to palladium, but only a weak absorption appeared in this region of the spectrum of the yellow complex, at 1 585 cm^{-1}. The Raman spectrum was therefore recorded, and showed a comparatively strong band at 1 586 cm^{-1}, readily assigned to the C=C stretch, together with broad Pd–Cl stretches at 328 and 306 cm^{-1}, in excellent agreement with the i.r. data. These results show the presence of a double bond different from that in free bbs, which may reasonably be assumed to be co-ordinated to palladium. This deduction is strongly supported by the i.r. results for [Pd(bbs)$_2$Cl$_2$] discussed in the following section, where the C=C stretch for the ligand co-ordinated through sulphur only is virtually identical with that for the free ligand.

It was difficult to confirm the presence of sulphur in the complex, so a detailed investigation was undertaken by *X*-ray photoelectron spectroscopy, a technique which has previously given valuable information on some palladium(II) and platinum(II) complexes.[15,16] Various model compounds including $[Pd(bbs)Cl_2]$, *cis*-$[Pd(PEt_2Ph)_2Cl_2]$, and $[Pd(bte)Cl_2]$ were also studied for comparison, and to support the validity of any conclusions reached. The absolute binding energies (eV) measured for some core levels of C, S, P, Pd, and Cl in these complexes are given in Table 2. In addition, the complexes showed either one or two oxygen 1*s* peaks, which from the binding energies appeared to be due to singly and doubly bonded oxygen respectively. These peaks are frequently found in the photoelectron spectra of inorganic compounds, and are caused by absorption of water or oxygen, and/or oxidation of readily oxidisable groups such as olefinic or phosphine ligands, on the surface of the material.

TABLE 2

Absolute binding energies (eV) for some core levels in palladium(II) complexes

Complex	Core level						
	C 1*s* [a]	C 1*s* π–π^*	Pd $3d_{\frac{3}{2}}$	Pd $3d_{\frac{5}{2}}$	S $2p_{\frac{3}{2}}$	Cl $2p_{\frac{3}{2}}$	P $2p_{\frac{1}{2}}$, $2p_{\frac{3}{2}}$
$[Pd(bbs)Cl_2]$	285.0	290	343.9	338.7	164.1	197.9	
$[Pd(bte)Cl_2]$	285.0	292	343.4	338.1	163.8	197.6	
cis-$[Pd(PEt_2Ph)_2Cl_2]$	285.0	292	343.6	338.3		197.6	131.2
$[Cl_2(Ph_3P)Pd(bbs)Pd(PPh_3)Cl_2]$	285.0	292	343.6	338.3	163.9	198.2	131.3

[a] Reference level.

The binding energies for Pd, S, Cl, and P are very similar throughout, as expected, and do not appear to vary significantly with the chemical environment. The presence of sulphur in the yellow product of the $[Pd(bbs)Cl_2]$–PPh_3 reaction is unequivocally confirmed, however. This complex is therefore assigned the structure $[Cl_2(Ph_3P)Pd(\mu\text{-}bbs)Pd(PPh_3)Cl_2]$, with a bridging but-3-enyl n-butyl sulphide ligand co-ordinated to one palladium through the sulphur and to the second palladium through the olefinic bond, in accordance with the vibrational-spectroscopic and analytical results.

TABLE 3

Atomic ratios calculated from the *X*-ray photoelectron spectroscopic results for some palladium(II) complexes

Complex		C	Pd	S	Cl	P
$[Pd(bbs)Cl_2]$	Calc.	8.0 ± 0.4	1	1.0 ± 0.05	2.0 ± 0.1	
	Theory	8	1	1	2	
$[Pd(bte)Cl_2]$	Calc.	10.0 ± 0.5	1	2.0 ± 0.1	2.0 ± 0.1	
	Theory	10	1	2	2	
cis-$[Pd(PEt_2Ph)_2Cl_2]$	Calc.	21 ± 1	1		2.0 ± 0.1	2.0 ± 0.1
	Theory	20	1		2	2
$[Cl_2(Ph_3P)Pd(bbs)Pd(PPh_3)Cl_2]$	Calc.	43 ± 2	2	1.0 ± 0.05	2.0 ± 0.1	1.0 ± 0.05
	Theory	44	2	1	2	1

This formulation is further supported by the atomic ratios for the complexes (Table 3), calculated from the peak intensities in the photoelectron spectra by allowing for variations in cross-section of the various core levels and instrumental characteristics. These were established by examining the spectra of a large number of palladium(II) complexes containing phosphine, chlorine, or sulphur ligands available in the laboratory, which were taken as standards. The complexes comprised $[Pd(SMe_2)_2Br_2]$, *trans*-$[Pd(PEt_2Ph)_2Cl_2]$, *trans*-$[Pd\{P(C_6H_{11})_3\}_2Cl_2]$, $[Pd(Ph_2PCH_2CH_2PPh_2)Cl_2]$, *cis*-$[Pd(PMe_3)_2Cl_2]$, $[Pd_2(C_3H_6)_2Cl_4]$, $[Pd_2(PBu_3)_2Cl_4]$, and $[Pd_2(PPr^{i}_3)_2Cl_4]$. (The palladium ratios were calculated from the spectra of the $3d_{\frac{5}{2}}$ core level.) The values in Table 3 are in excellent agreement with the structures of the complexes where known, and with the proposed structure of the new bbs complex.

An interesting feature of the photoelectron spectroscopic results is the energy value for the C 1*s* π–π^* shake-up transition in the complex $[Pd(bbs)Cl_2]$. This is appreciably lower than that found for a normal olefinic double bond,[17] as exemplified by $[Pd(bte)Cl_2]$ where the metal is co-ordinated *via* sulphur atoms only.[5] (This region of the photoelectron spectra for the two complexes with phenylphosphines present is dominated by the C 1*s* π–π^* transition of the aromatic groups,[18] so that no information regarding the olefinic bond in the new bridged complex can be deduced.) The result for $[Pd(bbs)Cl_2]$ probably reflects the attachment of the π system to palladium in this complex. Even so, the evidence presented is completely consistent with the proposed structure, and is difficult to rationalise in any other way.

There are four possible isomers for the bridged complex since the terminal chlorides may be all-*cis*, all-*trans*, *cis* at the sulphur end and *trans* at the alkene end, or *vice versa*. The vibrational-spectroscopic results clearly indicate the first of these configurations. Palladium(II) complexes containing terminal chlorines *trans* to other chlorines, including those with sulphur,[19,20] alkene,[21,22] and bridging co-ligands,[20–22] give strong Pd–Cl absorptions in their i.r. spectra between 340 and 370 cm^{-1}, usually at 355—360 cm^{-1}. This band also appears in the Raman spectra of unsymmetrical or bridged complexes.[22] No such bands were apparent in our spectra.

The observation of two Pd–Cl absorptions in both the Raman and i.r. spectra between 330 and 300 cm^{-1} is entirely consistent with a *cis* configuration for all the chlorines. Four Pd–Cl stretching frequencies might have been expected for an unsymmetrically bridged complex, but the values for the corresponding vibrations may well be very similar, since each palladium possesses the same set of terminal ligands. The Pd–Cl stretching frequencies for [Pd(bbs)Cl_2] are at 327 and 305 cm^{-1} (i.r.),[5] and 327 and 303 cm^{-1} (Raman), while for [Pd(nbd)Cl_2] the values are 338 and 304 cm^{-1} (i.r.) and 337 and 305 cm^{-1} (Raman).[23] The Raman spectrum was thus re-recorded under maximum resolution to try to separate each of the broad (*ca.* 10 cm^{-1} width at half-height) bands into two components. The lower-frequency band showed a possible shoulder at 304 cm^{-1}, but the less-intense band at higher frequency could not be clearly resolved. The configuration of the complex may nevertheless be assigned with some confidence as μ-(but-3-enyl n-butyl sulphide)-bis[*cis*-dichloro(triphenylphosphine)palladium(II)].

Reaction of Triethylphosphine with [Pd(bbs)Cl_2].—In an attempt to prepare a similar bridged complex with triethylphosphine as a ligand, which would confer better spectroscopic properties, the reaction of [Pd(bbs)Cl_2] and triethylphosphine (1 : 1) was investigated. Two different products were isolated, as described previously (Experimental section), suggesting that reaction (1)

$$2[\mathrm{Pd(bbs)Cl_2}] + 2\mathrm{PEt_3} \longrightarrow [\mathrm{Pd(PEt_3)_2Cl_2}] + [\mathrm{Pd(bbs)_2Cl_2}] \quad (1)$$

takes place. The stereochemistry of the solid product could not be deduced unambiguously from its i.r. spectrum; a medium-intensity band at 358 cm^{-1} suggested the presence of *trans*-[Pd(PEt_3)$_2$$Cl_2$],[24] but broad absorptions of similar intensity were also present between 307—320 and 280—293 cm^{-1}. The solid could indeed contain a mixture of both *cis* and *trans* isomers, as well as other palladium(II) complexes as impurities. The Raman spectrum was difficult to record, and showed only a very weak broad band in this region, centred at *ca.* 300 cm^{-1}.

The i.r. spectrum of the orange-red liquid showed a very strong absorption at 365 cm^{-1} in the Pd–Cl stretching region, indicating a *trans* structure for [Pd(bbs)$_2$$Cl_2$]. The products from the $PdCl_2$: bbs = 1 : 2 and [Pd(bbs)Cl_2] : bbs = 1 : 1 reactions gave absorptions at 367ms and 368vs cm^{-1}, together with a broad band centred at 303ms and 307m cm^{-1} respectively. The predominant species thus appears to be *trans*-[Pd(bbs)$_2$$Cl_2$] in each case, although again some of the *cis* isomer could be present, particularly from the reaction with $PdCl_2$ as the starting material. The configuration may thus depend on the preparative route.

In all cases, however, a single strong C=C band was seen, at 1 646 for the red liquid from the [Pd(bbs)Cl_2]–PEt_3 reaction, 1 644 from $PdCl_2$–2bbs, and 1 647 cm^{-1} from [Pd(bbs)Cl_2]–bbs. These compare with the value of 1 644 cm^{-1} found for freshly prepared bbs (lit.,[5] 1 635 cm^{-1}), and provide convincing evidence that the double bond of bbs is not co-ordinated to palladium in *trans*-[Pd(bbs)$_2$$Cl_2$]. A similar conclusion of co-ordination *via* the two sulphurs only was reached by Goodall[5] for the complex [Pd(bte)Cl_2] which gives a C=C absorption at 1 635s cm^{-1}, identical in frequency with that reported for the free ligand. These results provide strong support for the bridged structure deduced for [Cl_2(Ph_3P)Pd(μ-bbs)Pd(PPh_3)Cl_2] with the olefinic bond involved in co-ordination to one palladium. A bridging bbs group co-ordinated through sulphur only to both palladiums is expected to give a C=C absorption at a similar frequency to that of the free ligand, and not the observed shift of 50—60 cm^{-1}. It is also noteworthy that attempts to prepare palladium(II) complexes of the longer-chain unsaturated compound n-butyl pent-4-enyl sulphide (bps) led to the formation of brown oils from which no solids could be obtained,[5] although i.r. spectroscopy indicated the presence of unco-ordinated double bonds. If chelation is precluded by the larger ring size compared with bbs, complexes similar to [Pd(bbs)$_2$$Cl_2$] co-ordinated only through sulphur should result.

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REFERENCES

[1] K. B. Dillon, T. C. Waddington, and D. Younger, *J.C.S. Dalton*, 1975, 790.
[2] K. K. Chow, W. Levason, and C. A. McAuliffe, in 'Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan, London, 1973.
[3] Ya. M. Kimel'fel'd, E. M. Smirnova, N. I. Pershikova, O. L. Kaliya, O. N. Temkin, and R. M. Flid, *Russ. J. Struct. Chem.*, 1972, **13**, 581.
[4] L. F. Druding and S. I. Shupack, *J. Chromatog.*, 1966, **24**, 491.
[5] D. C. Goodall, *J. Chem. Soc.* (*A*), 1968, 887.
[6] A. Marbach and Y. L. Pascal, *Compt. rend.*, 1969, **C268**, 1074.
[7] D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *J. Organometallic Chem.*, 1972, **43**, 225.
[8] J. L. Spencer, M. Green, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1178.
[9] H. C. Clark and K. von Werner, *Synth. React. Inorg. Metal-Org. Chem.*, 1974, **4**, 355.
[10] A. W. Verstuyft and J. H. Nelson, *Synth. React. Inorg. Metal-Org. Chem.*, 1975, **5**, 69.
[11] G. B. Uffman, *Inorg. Synth.*, 1963, **7**, 236.
[12] H. Itatani and J. C. Bailar, jun., *J. Amer. Oil Chemists' Soc.*, 1967, **44**, 147.
[13] *Chem. Abs.*, 1972, **77**, formula index.
[14] M. J. Harriss, personal communication.
[15] D. T. Clark, D. Briggs, and D. B. Adams, *J.C.S. Dalton*, 1973, 169.
[16] D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Comm.*, 1971, 602.
[17] D. T. Clark and D. B. Adams, *Theor. Chim. Acta*, 1975, **39**, 321.
[18] D. T. Clark, D. B. Adams, A. Dilks, J. Peeling, and H. R. Thomas, *J. Electron Spectroscopy*, 1976, **8**, 51.
[19] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.
[20] D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1969, 588.
[21] R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 1897.
[22] G. F. Pregaglia, F. Conti, B. Minasso, and R. Ugo, *J. Organometallic Chem.*, 1973, **47**, 165.
[23] D. M. Adams and W. S. Fernando, *Inorg. Chim. Acta*, 1973, **7**, 277.
[24] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.