between 140 and 155° both conformations are possible when ligand **1** is used.

NMR Coupling Constants. Table IV shows NMR coupling constants between Ag and P ($^1J(^{107}Ag,^{31}P)$). Their changes are correlated to changes in structure: The coupling constants increase with decreasing Ag–P distance, increasing P–Ag–P angle, and decreasing nucleophilicity of the coordinating atom in the counterion. The trend is entirely analogous to results found for HgX_2L_2 compounds[24] (L stands for a variety of mono- and bidentate phosphine ligands, and X stands for a variety of anions). The trend in the coupling constants indicates an increase in the involvement of 5s orbitals of Ag in the bonding to P; the decrease in Ag–P distances suggests a concomitant strengthening of the Ag–P bond. The structures and coupling constants of **6** and **7** (Table IV) may also serve to explain data for $[AgCl(P(p\text{-}Tol)_3)_2]$ (**8**) and $[Ag_2Cl_2(PPh_3)_4]$ (**9**). The molecular weight of **8** determined from freezing point depression in benzene (at ~5 °C) indicates a monomeric structure.[25] The Ag–P coupling constant of 378 Hz determined at −80 °C[25] indicates a dimeric structure if it is compared to the values for **6** and **7** (399, 381 Hz). Indeed the crystal structure of **9** shows dimeric units[26] analogous to those observed for **6** and **7**. It would thus seem that at low temperature **8** associates into entropically more favorable dimers.

Acknowledgment. The ETH authors gratefully acknowledge financial support for this work from the Swiss National Science Foundation and S. Chaloupka for the preparation of some of the compounds.

Registry No. **2**, 59296-63-8; **3**, 86064-92-8; **4**, 86064-93-9; **5**, 86064-94-0; **6**, 60452-81-5; **7**, 52641-45-9.

Supplementary Material Available: Listings of positional and thermal parameters for all non-hydrogen atoms (Table S-I), calculated atomic coordinates for the hydrogen atoms (Table S-II), and calculated and observed amplitudes (Table S-III) (145 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Higher Oxidation States. 5.[1] Reaction of Palladium(II) Iodo Complexes with Molecular Iodine and Crystal and Molecular Structure of Diiodo(*cis*-1,2-bis(diphenylphosphino)ethylene)palladium(II)–Diiodine (1/1)

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Received September 30, 1982

The reactions of $[Pd(L\text{–}L)I_2]$ (L–L = $Me_2As(CH_2)_3AsMe_2$ (**1**), *cis*-$Ph_2PCH{=}CHPPh_2$ (**2**), *o*-$C_6H_4(SPh)_2$ (**3**)) with iodine produces the palladium(II) polyiodides $[Pd(L\text{–}L)I_4]$ (L–L = **1**, **2**) and $[Pd(L\text{–}L)I_3]$ (L–L = **3**). Similarly $[Pd(o\text{-}C_6H_4(AsMe_2)_2)_2I_2]$ is converted into $[Pd(o\text{-}C_6H_4(AsMe_2)_2)_2(I_3)_2]$. The crystal and molecular structure of $[Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)I_4]$ has been determined by X-ray diffraction (orthorhombic, space group *Pcab*, *a* = 16.424 (3) Å, *b* = 17.955 (6) Å, *c* = 20.545 (2) Å, *Z* = 8). The palladium atom is four-coordinate (P_2I_2 donor set, Pd–P = 2.252 (3), 2.244 (3) Å, Pd–I = 2.660 (1), 2.652 (1) Å) in a square-planar arrangement with adjacent groups being linked by I_2 molecules (I···I–I···I, I–I = 2.745 (1) Å, I···I = 3.527 (1), 3.483 (1) Å) to form approximately linear I_4 groups. The results are compared with the reactions of $[Pd(L\text{–}L)Cl_2]$ and $[Pd(L\text{–}L)Br_2]$ with the corresponding halogens, which in some cases lead to palladium(IV) complexes.

Introduction

We have recently reported[1,2] the synthesis and properties of a range of palladium(IV) chloro complexes containing neutral ligands, e.g. $[R_4N][PdLCl_5]$ (L = NMe_3, P-*n*-Pr_3, SMe_2), $[Pd(L\text{–}L)Cl_4]$ (L–L = $Me_2PCH_2CH_2PMe_2$, 2,2′-bipyridyl, $Ph_2PCH_2CH_2PPh_2$), and *trans*-$[Pd(L\text{–}L)_2Cl_2](ClO_4)_2$ (L–L = $Me_2PCH_2CH_2PMe_2$, *o*-$C_6H_4(PMe_2)(AsMe_2)$). A more restricted set of bromo complexes were also characterized, e.g. $[Pd(L\text{–}L)Br_4]$ (L–L = alkyldiphosphine or -diarsine).[1] Since the only established palladium(IV) iodo complex is the very recently reported[3] Cs_2PdI_6, the formation of iodopalladium(IV) complexes containing neutral ligands would be unexpected. However, a preliminary survey revealed that some $[Pd(L\text{–}L)I_2]$ reacted readily with molecular iodine, and hence a more detailed study was undertaken.

The reactions of platinum(II) iodo complexes of group 5B donor ligands with iodine gives products that depending upon the ligand and the conditions belong to one of the following classes: (i) platinum(IV) iodides, e.g. $[Pt(PMe_3)_2I_4]$[4] and $[Pt(Ph_2PCH_2CH_2PPh_2)I_4]$;[5] (ii) platinum(IV) polyiodides, e.g. $[Pt(o\text{-}phenanthroline)I_6]$;[6] (iii) mixed-valence class 2 compounds $[Pt(H_2NCH_2CH_2NH_2)_2][Pt(H_2NCH_2CH_2NH_2)_2I_2](ClO_4)_4$;[7] (iv) platinum(II) polyiodides, e.g. $[Pt(dimethylimidazole)_4](I_3)_2$[8] and $[Pt(TAAB)]I_8$[9] (TAAB = tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine). Several reports of palladium(II) polyiodides, e.g. $[Pd(TAAB)]I_8$,[9] $[Pd(NH_3)_4]I_8$,[10] and "partially oxidized" materials,[11,12] e.g.

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Pd(diphenylglyoximate)$_2$I$_x$, containing N-donor ligands have been published, but nothing seems to be known about analogues containing heavier group 5B donors.

Experimental Section

Physical measurements were made as described previously.[13] The palladium(II) complexes were made by literature methods: [Pd(Me$_2$NCH$_2$CH$_2$NMe$_2$)I$_2$],[14] [Pd(*cis*-Ph$_2$PCH=CHPPh$_2$)I$_2$],[15] [Pd(*o*-C$_6$H$_4$(SPh)$_2$)I$_2$],[16] [Pd(*o*-C$_6$H$_4$(SbPh$_2$)$_2$)I$_2$],[17] and Pd(*o*-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$I$_2$.[18]

Diiodo(1,3-bis(dimethylarsino)propane)palladium(II). A solution of sodium tetrachloropalladate(II) (0.4 g, 1 mmol) in ethanol (20 cm^3) was stirred for 3 h with sodium iodide (1 g), and the ligand (0.25 g, 1 mmol) was added. After a further 3 h the solution was evaporated to dryness, the product extracted with dichloromethane (100 cm^3), and the complex obtained by precipitation with diethyl ether. Anal. Calcd for $C_7H_{18}As_2I_2Pd$: C, 13.75; H, 3.0. Found: C, 14.0; H, 2.9.

Reaction of [Pd(L–L)I$_2$] with Molecular Iodine. General Method. A concentrated dichloromethane solution of [Pd(L–L)I$_2$] (1 mmol) (L–L = *cis*-Ph$_2$PCH=CHPPh$_2$, Me$_2$NCH$_2$CH$_2$NMe$_2$, Me$_2$As(CH$_2$)$_3$AsMe$_2$) was mixed with a solution of iodine (1.2 g, 4 mmol) in the same solvent. The solution was filtered and cooled in a refrigerator for 2–6 days. The crystals that were produced were filtered off and dried in vacuo. The reactions with [Pd(L–L)I$_2$] (L–L = *o*-C$_6$H$_4$(SbPh$_2$)$_2$, *o*-C$_6$H$_4$(SPh)$_2$) were conducted similarly in 1,2-dichloroethane.

[Pd(Me$_2$As(CH$_2$)$_3$AsMe$_2$)I$_4$]. Anal. Calcd for $C_7H_{18}As_2I_4Pd$: C, 9.7; H, 2.1; I, 58.6. Found: C, 10.1; H, 2.25; I, 59.6. E_{max} (diffuse reflectance (dr), ×10^3 cm^{-1}): 28.4, 22.6, 18.5 sh, 16.4 sh. E_{max} (CH$_2$Cl$_2$, ×10^3 cm^{-1}): 26.7, 22.6, 21.3 sh.

[Pd(*cis*-Ph$_2$PCH=CHPPh$_2$)I$_4$]. Anal. Calcd for $C_{26}H_{22}I_4P_2Pd$: C, 30.9; H, 2.2; I, 50.3. Found: C, 30.7; H, 2.1; I, 50.0. E_{max} (dr, ×10^3 cm^{-1}): 23.0, 21.3 sh, 18.2 sh. E_{max} (CH$_2$Cl$_2$, ×10^3 cm^{-1}): 29.7 sh, 24.4, 21.1.

[Pd(*o*-C$_6$H$_4$(SbPh$_2$)$_2$)I$_2$]. Anal. Calcd for $C_{30}H_{24}I_2PdSb_2$: C, 36.4; H, 2.2. Found: C, 36.4; H, 2.0.

[Pd(Me$_2$NCH$_2$CH$_2$NMe$_2$)I$_2$]. Anal. Calcd for $C_6H_{16}I_2N_2Pd$: C, 15.1; H, 3.4. Found: C, 15.3; H, 3.5.

[Pd(*o*-C$_6$H$_4$(SPh)$_2$)I$_3$]. Anal. Calcd for $C_{18}H_{14}I_3PdS_2$: C, 27.7; H, 1.8; I, 48.7. Found: C, 27.4; H, 1.9; I, 49.2.

Pd(*o*-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$I$_6$. A suspension of Pd(*o*-C$_6$H$_4$(AsMe$_2$)$_2$)$_2$I$_2$ (0.93 g, 1 mmol) in CH$_2$Cl$_2$ (20 cm^3) was refluxed for 3 h with iodine (1.2 g, 4 mmol); the initially red-brown solid darkened, and finally a fine black material was produced. This was filtered off, rinsed with CH$_2$Cl$_2$, and dried in vacuo. The yield was ca. quantitative. Anal. Calcd for $C_{20}H_{32}As_4I_6Pd$: C, 16.6; H, 2.2; I, 52.9. Found: C, 16.8; H, 2.0; I, 53.3.

[Pd(*cis*-Ph$_2$PCH=CHPPh$_2$)Cl$_4$] was prepared by chlorine oxidation of [Pd(*cis*-Ph$_2$PCHCHPPh$_2$)Cl$_2$][15] suspended in CCl$_4$ as described previously[1] for other [Pd(L–L)Cl$_4$] complexes. Anal. Calcd for $C_{26}H_{22}Cl_4P_2Pd$: C, 48.5; H, 3.4. Found: C, 48.7; H, 3.5. E_{max} (dr, ×10^3 cm^{-1}): 20.8, 25.4, 28.7.

X-ray Crystal Structure Determination. Slow cooling to ∼−20 °C of a mixture of [Pd(*cis*-Ph$_2$PCHCHPPh$_2$)I$_2$] and I$_2$ (1:4 mole ratio) in methylene chloride gave air-stable black crystals which for X-ray examination were mounted in Lindemann capillaries. Preliminary photographic examination established the crystal system and approximate cell dimensions, and precise cell dimensions were obtained for 25 accurately centered reflections on an Enraf-Nonius CAD-4 diffractometer.

Crystal Data: $C_{26}H_{22}I_4P_2Pd$ ≡ [Pd(Ph$_2$PCHCHPPh$_2$)I$_4$], fw = 1010.4, orthorhombic, a = 16.424 (3) Å, b = 17.955 (6) Å, c = 20.545 (2) Å, V = 6058.6 Å^3, Z = 8, D(calcd) = 2.215 g cm^{-3}, D(obsd by flotation) = 2.21 (2) g cm^{-3}, F(000) = 3728, μ(Mo Kα) = 47.3 cm^{-1}, λ(Mo Kα) = 0.7107 Å. Systematic absences hkl (none), $hk0$ ($k \neq 2n$), $h0l$ ($h \neq 2n$), and $0kl$ ($l \neq 2n$) lead to the unique centrosymmetric space group *Pcab* (No. 61).

Collection and Reduction of Diffractometer X-ray Data. Diffraction data were recorded on a CAD-4 diffractometer fitted with graphite-monochromated Mo Kα radiation with use of a room-temperature crystal (0.05 × 0.20 × 0.30 mm). A total of 5320 unique reflections were recorded (1.5° ≤ θ ≤ 25°). The check reflections showed no deterioration during the course of the experiment, the data were corrected for Lorentz and polarization effects, and an empirical ψ scan absorption correction was applied. (transmission: minimum, 0.77; maximum, 1.00). Removing 2110 reflections where $F \leq 2\sigma(F)$ left 3210 reflections which were regarded as observed and used in the structure determination and refinement.

Solution and Refinement of the Structure. The positions of the Pd and I atoms were determined by direct methods. The E map derived from the most probable solution showed five prominent peaks which were fully consistent with the Patterson map. Repeated structure factor and electron density calculations readily located the remaining non-hydrogen atoms. Least-squares refinement (isotropic atoms, rigid phenyl groups (d(C–C) = 1.395 Å)) reduced R_1 to 0.0970. An empirical weighting scheme $w = 1/(\sigma^2(F) + AF_o^2)$ was introduced where A (0.0003) was chosen to make $w\Delta^2$ independent of F_o. Allowing the heavy atoms (Pd, I, P) to have anisotropic temperature factors and introducing H atoms in calculated positions (d(C–H) = 1.08 Å) gave a converged R_1 of 0.0753 (121 parameters). The large linear absorption coefficient for the material indicated that the absorption correction would be important, and an alternative empirical method developed by Walker and Stuart[19] was used. This yielded, for the same model as above, virtually identical results both in the R factors (R_1 = 0.0748) and in the atomic parameters, and since there were no obvious benefits of this procedure, it was not further pursued. Introducing anisotropic carbon atoms into the model caused a small but highly significant decrease in the R factors when the Hamilton statistical test[20] was applied. Full-matrix least squares (251 parameters, anisotropic Pd, I, P, C atoms, rigid phenyl groups, hydrogen atoms in calculated positions (d(C–H) = 1.08 Å), empirical weights ($w = 1/(\sigma^2(F) + 0.0003F_o^2)$) converged to R_1 = 0.0722, R_2 = 0.0471 ($R_1 = \sum(\Delta F)/\sum F_o$, $R_2 = (\sum w(\Delta F)^2/\sum wF_o^2)^{1/2}$).

A difference electron density synthesis calculated toward the end of the refinement showed no significant features (−1.42 ≤ electron density ≤ 1.47 e Å^{-3}). There are as expected from the structure a number of very large structure factors, but no attempt was made to include extinction in the model. The origin of the disparity between R_1 and R_2 is not clear, but inspection of the structure factor list showed no gross anomalies.

Atomic scattering factors for neutral atoms and the anomalous dispersion corrections were taken from SHELX[21] (P, C, H) and ref 22 (Pd, I). All calculations were performed on an ICL2970 computer at the University of Southampton using the programs SHELX,[21] PLUTO,[23a] ORTEP,[23b] and XANADU.[24] The final non-hydrogen positional parameters are presented in Table I.

Results and Discussion

The reactions of five representative [Pd(L–L)I$_2$] complexes (L–L = Me$_2$NCH$_2$CH$_2$NMe$_2$, Me$_2$As(CH$_2$)$_3$AsMe$_2$, *cis*-

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Table I. Atomic Coordinates ($\times 10^4$) for Pd(*cis*-$Ph_2PCHCHPPh_2$)I_4[a]

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Pd	459 (1)	364 (0)	2725 (0)	C(23)	3104 (5)	2145 (4)	1794 (4)
I(1)	−441 (1)	847 (0)	1735 (0)	C(24)	2690 (5)	2729 (4)	2096 (4)
I(2)	−730 (0)	441 (1)	3596 (0)	C(25)	1925 (5)	2606 (4)	2372 (4)
I(3)	−509 (1)	2384 (1)	3416 (1)	C(26)	1574 (5)	1899 (4)	2344 (4)
I(4)	−481 (1)	3907 (1)	3299 (1)	C(31)	1528 (5)	672 (4)	4124 (4)
P(1)	1590 (2)	385 (2)	2105 (1)	C(32)	2175 (5)	1151 (4)	3989 (4)
P(2)	1286 (2)	−25 (2)	3526 (1)	C(33)	2380 (5)	1712 (4)	4430 (4)
C(1)	2397 (7)	−80 (6)	2545 (6)	C(34)	1938 (5)	1794 (4)	5005 (4)
C(2)	2275 (7)	−239 (7)	3161 (6)	C(35)	1290 (5)	1315 (4)	5139 (4)
C(11)	1608 (5)	−16 (5)	1304 (3)	C(36)	1085 (5)	755 (4)	4699 (4)
C(12)	1753 (5)	−779 (5)	1247 (3)	C(41)	1021 (5)	−875 (4)	3930 (4)
C(13)	1689 (5)	−1126 (5)	642 (3)	C(42)	1348 (5)	−1060 (4)	4536 (4)
C(14)	1479 (5)	−710 (5)	94 (3)	C(43)	1207 (5)	−1763 (4)	4802 (4)
C(15)	1333 (5)	52 (5)	150 (3)	C(44)	738 (5)	−2281 (4)	4462 (4)
C(16)	1398 (5)	400 (5)	756 (3)	C(45)	411 (5)	−2096 (4)	3857 (4)
C(21)	1988 (5)	1316 (4)	2042 (4)	C(46)	552 (5)	−1394 (4)	3591 (4)
C(22)	2752 (5)	1438 (4)	1767 (4)				

[a] In this and the subsequent table the estimated standard deviations are given in parentheses. The carbon atoms of the phenyl groups are labeled C(*IJ*), where *I* (1–4) indicates the ring and *J* (1–6) the atoms within a ring.

Table II. Selected Bond Lengths (Å) and Angles (deg) for Pd(*cis*-$Ph_2PCHCHPPh_2$)I_4[a]

Pd–I(1)	2.660 (1)	I(2)–I(3)	3.527 (1)
Pd–I(2)	2.652 (1)	I(3)–I(4)	2.745 (1)
Pd–P(1)	2.252 (3)	I(4)–I(1′)	3.483 (1)
Pd–P(2)	2.244 (3)	C(1)–C(2)	1.314 (16)
P(1)–C(1)	1.808 (11)	P(2)–C(2)	1.830 (11)
P(1)–C(11)	1.797 (8)	P(2)–C(31)	1.799 (8)
P(1)–C(21)	1.798 (7)	P(2)–C(41)	1.791 (8)
I(1)···I(2)	3.92	I(1)···P(1)	3.52
P(1)···P(2)	3.05	I(2)···P(2)	3.42
I(1)–Pd–I(2)	95.1 (1)	I(1)–Pd–P(1)	91.2 (1)
P(1)–Pd–P(2)	85.5 (1)	I(2)–Pd–P(2)	88.1 (1)
Pd–P(1)–C(1)	108.3 (4)	Pd–P(2)–C(2)	107.6 (4)
Pd–P(1)–C(11)	121.6 (3)	Pd–P(2)–C(31)	114.7 (3)
Pd–P(1)–C(21)	110.9 (3)	Pd–P(2)–C(41)	117.3 (3)
C(1)–P(1)–C(11)	105.1 (5)	C(2)–P(2)–C(31)	103.3 (5)
C(1)–P(1)–C(21)	101.5 (5)	C(2)–P(2)–C(41)	103.0 (5)
C(11)–P(1)–C(21)	107.4 (4)	C(31)–P(2)–C(41)	109.3 (4)
P(1)–C(1)–C(2)	118.1 (9)	P(2)–C(2)–C(1)	118.9 (9)
Pd–I(2)–I(3)	84.6 (1)	I(3)–I(4)–I(1′)	176.1 (1)
I(2)–I(3)–I(4)	174.9 (1)	I(4)–I(1′)–Pd′	72.6 (1)

[a] Primed atoms are related to unprimed atoms by *x*, $^1/_2 + y$, $^1/_2 - z$.

$Ph_2PCH{=}CHPPh_2$, *o*-$C_6H_4(SbPh_2)_2$, and *o*-$C_6H_4(SPh)_2$) with excess molecular iodine was carried out under standardized conditions, essentially by mixing concentrated solutions of [Pd(L–L)I_2] and I_2 ([Pd(L–L)I_2]:I_2 = 1:4 mole ratio, Pd:total I = 1:10) in CH_2Cl_2 or $C_2H_4Cl_2$ at room temperature and cooling to −20 °C. In two cases, L–L = $Me_2NCH_2CH_2NMe_2$, *o*-$C_6H_4(SbPh_2)_2$, the palladium(II) starting material was recovered unchanged, but in the other cases black materials of higher iodine content were obtained. Analytical data were consistent with the formulations [Pd(L–L)I_4] (L–L = $Me_2As(CH_2)_3AsMe_2$, *cis*-$Ph_2PCH{=}CHPPh_2$) and Pd(*o*-$C_6H_4(SPh)_2$)I_3, respectively.

Structural Studies. Initial attempts at X-ray crystallographic studies were made on crystals of [Pd($Me_2As(CH_2)_3AsMe_2$)I_4], but these lost iodine very easily even in sealed capillaries, and preliminary photographic work showed extensive decomposition. This work was terminated, and studies were switched to [Pd(*cis*-$Ph_2PCHCHPPh_2$)I_4], which showed no deterioration on storage at room temperature or during data collection. The atom-numbering scheme is shown in Figure 1, and selected bond lengths and angles are given in Table II. The structure consists of an essentially square-planar arrangement about each palladium atom composed of two iodine atoms, and two phosphorus atoms of the chelating diphosphine. These are linked into chains by molecules of iodine linking iodine atoms of neighboring molecules as shown in Figures 1 and 2. The packing diagram (Figure 2) shows the polymeric nature of the structure and the groups of four iodine atoms lying approximately in the *y* direction.

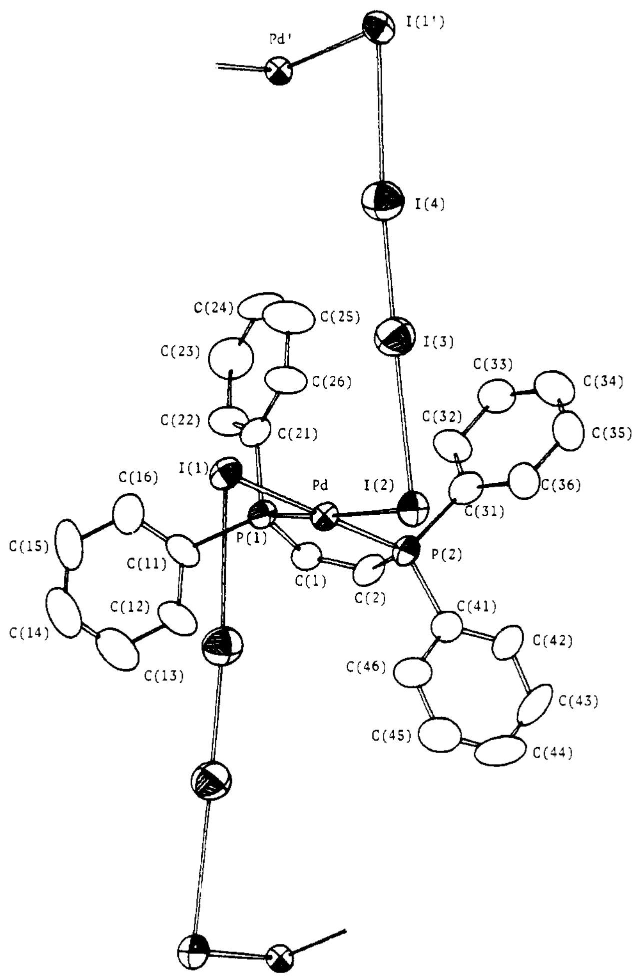

Figure 1. View of [Pd(*cis*-$Ph_2PCHCHPPh_2$)I_4] showing the coordination around one palladium atom, the linking of iodine atoms into I_4 chains, and the atom-numbering system. The atoms are drawn with 50% probability thermal ellipsoids.

Considering the palladium environment first, the planar four-coordination immediately suggests palladium(II) (d^8) rather than the d^6 palladium(IV), which is invariably octa-

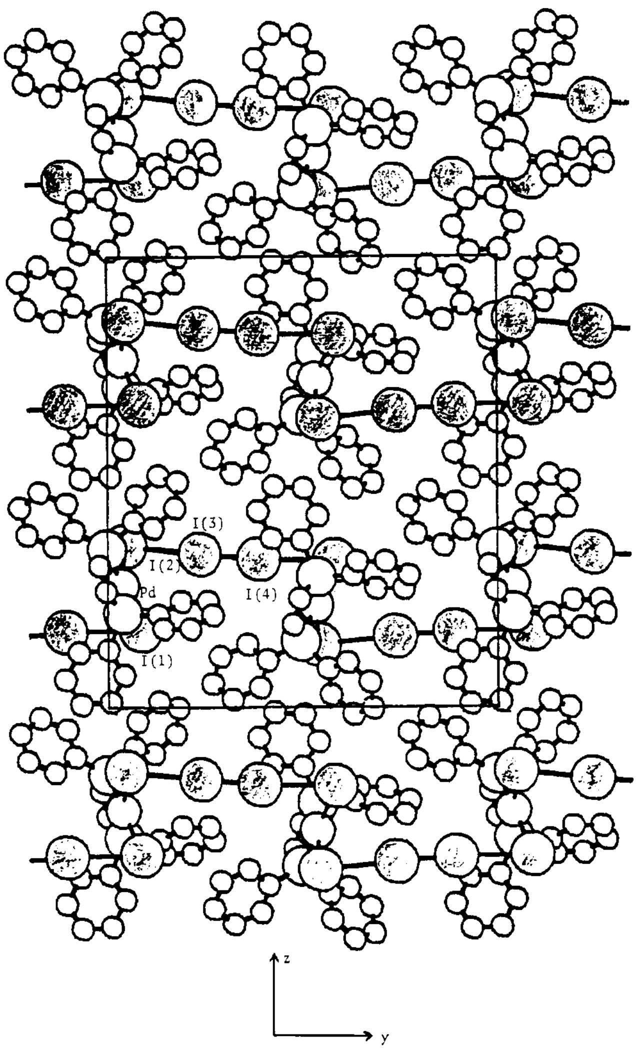

Figure 2. Partial packing diagram for [Pd(*cis*-$Ph_2PCHCHPPh_2$)I_4] viewed from the *a* direction ($x/a \approx 0.0$–0.5).

hedrally coordinated.[25] The Pd–I bond lengths 2.660 (1), 2.652 (1) Å are similar to the Pd–I_{transP} bond length in [Pd-(*o*-$C_6H_4(PPh_2)(SMe)$)I_2][26] (2.658 (1) Å) and are significantly longer than the Pd–I_{transI} bonds in *trans*-[Pd(PPh_3)$_2I_2$] (2.587 (1) Å)[27] or *trans*-[Pd(PMe_2Ph)$_2I_2$] (2.611, 2.587 (6) Å),[28] consistent with the expected high trans influence of phosphorus. The Pd–P bond lengths 2.252 (3) and 2.244 (3) Å are in good agreement with that in [Pd(*o*-$C_6H_4(PPh_2)(SMe)$)I_2][26] (2.250 (2) Å) and are somewhat longer than the Pd–$P_{transCl}$ bonds in [Pd($Ph_2PCH_2CH_2PPh_2$)Cl_2] (2.233 (2), 2.226 (2) Å).[29] The P–Pd–P angle (85.5°) is comparable with that in [Pd-($Ph_2PCH_2CH_2PPh_2$)Cl_2] (85.8°).[29] The dimensions of the diphosphine ligand (L–L) are unexceptional and agree well with those reported in [Hg(L–L)Br_2],[30] [Fe(L–L)$_2Cl_2$],[31] and [Fe(L–L)$_2Br_2$].[32] The P—C=C angles (~118°) are very close to the idealized 120° value, the PCCP torsion angle is 3.05°, and the angle between the PC=CP plane and the PdP_2 plane is 11.45°. The general impression is that despite the relatively rigid ligand backbone there is little strain in the molecule.

The most interesting feature of the structure involves the polyiodide units. These can be described as above as $I^- \cdots I–I \cdots I^-$ or alternatively as bridging I_4^{2-} ligands. The I_4^{2-} ion has been identified in [Co(NH_3)$_6$](I_3)(I_4)[33] and is weakly coordinated in Cu(NH_3)$_4I_4$[33] and strongly bound in [Cd(NH_3)$_4I_4$],[33] [Pt(*o*-phenanthroline)I_5], and [Pt(*o*-phenanthroline)I_6].[6] In all examples the I_4 unit is approximately linear, the largest deviation being in the Pt(IV) complexes ~16° and in [Pd-(*cis*-$Ph_2PCHCHPPh_2$)I_4] is ~5°. In general the distances between the central iodines (~2.74–2.83 Å) are slightly greater than in solid molecular iodine (2.715 Å)[33] and the $I^- \cdots I_2$ distances are 3.30–3.45 Å, indicative of weak bonds. The $I^- \cdots I_2$ distances in [Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_4] (3.48, 3.53 Å) are the longest yet reported for discrete I_4^{2-} groups, and the I–I (2.745 (1) Å) is among the shortest, which is interpreted as evidence for weaker $I^- \cdots I_2$ interaction in the present example. The arrangement of the I_4 chains in the present complex is unique and differs from that found in the Pt(IV) complexes or [Cd(NH_3)$_4I_4$], where they are positioned trans across the metal center. There are no close approaches to other iodine atoms.

Physical Measurements. The [Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_4] complex is a nonelectrolyte in 10^{-3} M $C_2H_4Cl_2$, and its electronic spectrum in this solvent can be reproduced closely (but not exactly) by superimposing the spectra of [Pd(*cis*-$Ph_2PCH{=}CHPPh_2$)I_2] and iodine, suggesting extensive dissociation in solution. This dissociation is in keeping with the weak $I^- \cdots I_2$ interaction demonstrated by the X-ray results. The diffuse-reflectance spectrum of the solid complex consists of very broad intense absorption. The properties of [Pd($Me_2As(CH_2)_3AsMe_2$)I_4] and [Pd(*o*-$C_6H_4(SPh)_2$)I_3] are generally very similar to those of the diphosphine complex, although the diarsine loses iodine much more readily. These too are regarded as palladium(II) polyiodides.

Pd(*o*-$C_6H_4(AsMe_2)_2$)$_2I_6$. Attempts to isolate an adduct by cooling saturated solutions of [Pd(*o*-$C_6H_4(AsMe_2)_2$)$_2I_2$][18] and I_2 in CH_2Cl_2 were unsuccessful due to the poor solubility of the Pd(II) complex. However, when a suspension of the material in CH_2Cl_2 with a four-fold excess of I_2 was refluxed, the black Pd(*o*-$C_6H_4(AsMe_2)_2$)$_2I_6$ was produced. This complex is insoluble in halocarbons but dissolves readily in acetonitrile, where it behaves as a 1:2 electrolyte, $\Lambda_{10^{-3}M} = 270\ \Omega^{-1}\ cm^2\ mol^{-1}$,[34] and its electronic spectrum is dominated by two very intense absorptions at 28 800 cm^{-1} ($\epsilon_{mol} \simeq 40\,000\ dm^3\ mol^{-1}\ cm^{-1}$) and 34 500 cm^{-1} ($\epsilon_{mol} \simeq 80\,000$) characteristic[35] of the I_3^- ion. In solution therefore the material is formulated [Pd(*o*-$C_6H_4(AsMe_2)_2$)$_2$](I_3)$_2$. The solid reflectance electronic spectrum contains intense absorptions with poorly defined maxima, 20 000–40 000 cm^{-1}, but is similar in profile to the reflectance spectra of CsI_3 and Et_4NI_3,[35] suggesting the I_3 groups retain their integrity.

In the solid state the structure is probably composed of planar [Pd(*o*-$C_6H_4(AsMe_2)_2$)$_2$]$^{2+}$ ions with I_3^- ions completing a very distorted tetragonal arrangement, similar to that found in [Pd(*o*-$C_6H_4(AsMe_2)_2$)$_2I_2$].[36]

Conclusion

The above results show that in the cases studied the reaction of palladium(II) iodo complexes of group 5B and 6B ligands

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leads to Pd(II) polyiodides rather than Pd(IV) complexes. It is interesting to recall that $[Pd(o\text{-}C_6H_4(AsMe_2)_2)X_2]$ and $[Pd(Me_2As(CH_2)_3AsMe_2)X_2]$[1] (X = Cl, Br) give Pd(IV) complexes on halogen oxidation. Chlorination of $[Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)Cl_2]$ also produces the Pd(IV) analogue (Experimental Section), but $[Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)Br_2]$ does not react with Br_2, behavior identical with that reported for the Pd(II) complexes of $Ph_2PCH_2CH_2PPh_2$.[1] The $[Pd(L\text{-}L)X_2]$ (X = Cl, Br) complexes of the dithioether ligand do not oxidize on treatment with halogen.[13]

Acknowledgment. The authors wish to thank Dr. M. B. Hursthouse for X-ray data collection on the SERC/QMC Enraf-Nonius CAD-4 diffractometer and the University of Southampton for financial support (D.J.G. and L.R.G.).

Registry No. $Pd(Me_2As(CH_2)_3AsMe_2)I_2$, 86272-79-9; $Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)I_2$, 57255-07-9; $Pd(Me_2NCH_2CH_2NMe_2)I_2$, 86272-80-2; $Pd(o\text{-}C_6H_4(SbPh_2)_2)I_2$, 61872-22-8; $Pd(o\text{-}C_6H_4(SPh)_2)I_2$, 71499-01-9; $Pd(Me_2As(CH_2)_3AsMe_2)I_4$, 86272-81-3; $Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)I_4$, 86272-82-4; $Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)Cl_4$, 86272-83-5; $Pd(cis\text{-}Ph_2PCH{=}CHPPh_2)Cl_2$, 57255-05-7; $Pd(o\text{-}C_6H_4(AsMe_2)_2)_2I_6$, 86272-84-6; $Pd(o\text{-}C_6H_4(AsMe_2)_2)_2I_2$, 59110-23-5.

Supplementary Material Available: Tables III–VI giving isotropic and anisotropic temperature factors, H atom coordinates, equations of planes, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Contribution from the Molecular Structure Center and Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Isolation and Molecular Structures of Dinuclear $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$ and Cubane-like $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$, Two Oligomers in Equilibrium

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Received October 21, 1982

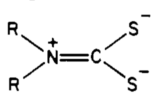
The reaction of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ and $S_2CN(i\text{-}C_4H_9)_2^-$ produces yellow $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$ and red $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$. The dinuclear compound crystallizes in the space group $P2_1/c$ with $a = 17.73$ (1) Å, $b = 9.805$ (5) Å, $c = 22.89$ (2) Å, $\beta = 91.45$ (3)°, and $Z = 4$. Final residuals were $R(F) = 0.063$ and $R_w(F) = 0.055$. The tetranuclear compound crystallizes in the space group $P2_1/n$ with $a = 18.15$ (1) Å, $b = 17.64$ (1) Å, $c = 25.63$ (1) Å, $\beta = 105.12$ (3)°, and $Z = 4$. Final residuals were $R(F) = 0.079$ and $R_w(F) = 0.079$. The structure of the former is similar in many respects to those of $[MoX(\mu\text{-}S)L]_2$ (X = O, S; L = bidentate ligand) while the $[Mo(\mu_3\text{-}S)]_4$ core of the latter mimics that found in the cubane-like $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ complex. The equilibrium between the oligomers in solution is supported both by their isolation from the same reaction mixture and by spectroscopic evidence.

Introduction

The isolation[1] and structural characterization[2] of the cubane-like tetranuclear compound $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ were reported previously. These results are noteworthy and unusual because the authenticated[3] structure of $[MoO(\mu\text{-}S)(S_2P(O\text{-}i\text{-}C_3H_7))_2]_2$ indicates that the existing analogies[4] in the structures of mononuclear arylimido and oxo compounds do not necessarily persist with polynuclear compounds. The tetranuclear nature of the arylimido compound was also defined by a molecular weight measurement for a rather concentrated solution.[1] In dilute solutions, however, the absorbances arising from a band at 585 nm deviate from the Beer–Lambert law in such a way that the equilibrium in eq 1 was postulated to account for the deviation.[1]

$$2[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2 \rightleftharpoons [Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4 \quad (1)$$

With the link between the degree of oligomerization and the identity of the multiply bound terminal ligand (O or NR) at least tentatively established (but with further examination clearly required), the influence of the bidentate ligand on the degree of oligomerization presented the next challenge that we wished to address. If the dithiophosphate ligands of the arylimido compound were replaced by dithiocarbamate ligands, the identity of the immediate coordination environment about each metal atom would be unchanged but other influences would be altered drastically. The valence angles around the phosphorus atoms of the dithiophosphate ligands force one of each pair of alkyl substituents to lie along the Mo–S bonds which are reponsible for binding two dinuclear molecules into a tetranuclear unit. The expected planar skeletons of the dithiocarbamate ligands would result in substantially lessened steric effects and provide a measure of increased stability for a tetranuclear compound. However, the resonance form given by **1**, whose importance would be evident from the planarity



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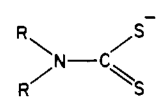
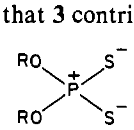


2

of the skeleton, should provide more electron density to each metal atom than **2** and its equivalent canonical form. The additional electron density would be expected to enhance the stability of the dinuclear compound since it can be utilized by the empty orbital on each molybdenum atom. In contrast, we do not believe that **3** contributes significantly to the stability



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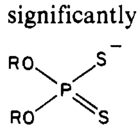

4

of the dinuclear dithiophosphate compound. The importance of multiple bonding at the phosphorus atom leads us to believe that **4** and its equivalent canonical form would make a much larger contribution.

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