Reactions of Carbodi-imides with Palladium(II) Compounds

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New dihalogenobis(carbodi-imide)palladium(II) compounds are formed in the reactions between di-t-butyl- and methyl-t-butylcarbodi-imides and (PhCN)$_2$PdX$_2$ (X = Cl and Br) in dichloromethane solution. In methanol solution, 1,2-addition of solvent to di-*o*-tolyl-, dicyclohexyl-, and methyl-t-butylcarbodi-imides is promoted by Pd^{II}, and dihalogenobis(isourea) complexes are obtained. Structures of the compounds are discussed on the basis of i.r. and ^{1}H n.m.r. observations.

THEORETICALLY, ligands containing hetero-multiple-bond systems C=N are capable of co-ordination to a transition metal either through the nitrogen lone pair or through the π-system. Evidence for π-co-ordination has been obtained from *X*-ray diffraction studies of (PhCH:CH·CH:NPh)Fe(CO)$_3$,[1] where the bonding of the unsaturated imine ligand is similar to that found in conjugated diolefins, and of (Ph$_2$C:C:NMe)Fe$_2$(CO)$_6$,[2] where the heterocumulenic system occupies a bridging position with a bent CCN unit π-bonded to one iron atom in an analogous manner to a π-allyl group and the second iron atom attached to the C=N unit. Co-ordination through the nitrogen lone pairs occurs, however, for the chelating di-imine system in (PhN:CMe·CMe:NPh)-Fe(CO)$_3$.[3] Similar possibilities of σ- or π-co-ordination clearly also exist for carbodi-imides, RN:C:NR′ (R,R′ = alkyl and aryl).

Carbodi-imide–transition metal reactions were also of interest to us because of the observed high reactivity of the 1,2-dipole of carbodi-imides in insertion reactions into a variety of M–X bonds (*e.g.* M = B or Al, X = Cl or Br).[4] Specifically, the formation of di-μ-chloro-di-π-(2-chloroprop-2-enyl)dipalladium(II) in the reaction between allene and dichlorobis(benzonitrile)palladium(II), which is probably an example of an insertion reaction of a double bond between a Pd–Cl bond,[5] encouraged us to explore the reactions of carbodi-imides with palladium(II) systems. In addition to the possibility of obtaining similar chloro-bridged species, the possible formation of binuclear complexes bridged by a chloroformamidine (RN:CCl·NR′) unit, analogous to the complexes, Pd$_2$(dpt)$_4$, isolated from the reactions between the anion (dpt) formed from the deprotonation of 1,3-diphenyltriazene, and palladium(II) systems,[6] was also considered.

RESULTS AND DISCUSSION

Reactions between di-t-butyl- and methyl-t-butyl-carbodi-imides and *trans*-(PhCN)$_2$PdX$_2$ (X = Cl and Br) in CH$_2$Cl$_2$ solution gave good yields of monomeric, non-ionic, and diamagnetic complexes of stoicheiometry L$_2$PdX$_2$ (L = carbodi-imide). The retention of the characteristic absorption around 2130 cm^{-1} assigned[7] to the antisymmetric stretching vibration of the N:C:N system indicates that the carbodi-imide molecule has remained intact in the complex, and rules out the possibility of an insertion reaction. It also suggests that π-interaction does not occur since a significant lowering in the energy of the absorption would be expected. In fact for methyl-t-butylcarbodi-imide there is a slight shift to higher energy which, on the basis of an observed increase of the C:N stretching frequency of alkyl cyanides co-ordinated through the nitrogen lone pair,[8] indicates that similar co-ordination has occurred in this case. In keeping with their non-ionic and diamagnetic nature, these L$_2$PdX$_2$ compounds are most probably square-planar, and the observation of only one absorption in the Pd–X stretching region of the i.r. spectrum (Table 1)

TABLE 1

I.r. Absorptions (cm^{-1}) for L$_2$PdX$_2$ complexes [L = carbodi-imide; X = Cl or Br]

Compound	ν(N=C=N) [a]	ν(Pd–X) [b]
(MeN:C:NBu^t)$_2$PdCl$_2$	2143s	344m
(MeN:C:NBu^t)$_2$PdBr$_2$	2140s	254m
MeN:C:NBu^t	2127s	
(Bu^{t}N:C:NBu^t)$_2$PdCl$_2$	2128s, 2092m	340m
(Bu^{t}N:C:NBu^t)$_2$PdBr$_2$	2126s, 2093m	261m
Bu^{t}N:C:NBu^t	2126s, 2105s, 2094s	

[a] In CHCl$_3$ solution. [b] Nujol mulls

TABLE 2

^{1}H N.m.r. data for carbodi-imides and carbodi-imide complexes (chemical shifts relative to internal benzene in benzene solution, and to internal Me$_4$Si in CDCl$_3$ solution)

Compound	Solvent	τMe	τBu^t
Bu^{t}N:C:NBu^t	C$_6$H$_6$		8·98
	CDCl$_3$		8·71
(Bu^{t}N:C:NBu^t)$_2$PdCl$_2$	C$_6$H$_6$		8·63, 8·86
[(Bu^{t}N:C:NBu^t)PdCl$_2$]$_2$	C$_6$H$_6$		8·94, 9·09
(Bu^{t}N:C:NBu^t)$_2$PdCl$_2$	CDCl$_3$		8·46,[a] 8·52 [a]
(Bu^{t}N:C:NBu^t)$_2$PdBr$_2$	C$_6$H$_6$		8·63, 8·87
[(Bu^{t}N:C:NBu^t)PdBr$_2$]$_2$	C$_6$H$_6$		8·94, 9·08
(Bu^{t}N:C:NBu^t)$_2$PdBr$_2$	CDCl$_3$		8·47,[a] 8·51 [a]
MeN:C:NBu^t	CDCl$_3$	7·00	8·70
(MeN:C:NBu^t)$_2$PdCl$_2$	CDCl$_3$	6·80, 7·00	8·44, 8·55
(MeN:C:NBu^t)$_2$PdBr$_2$	CDCl$_3$	6·84, 7·00	8·47, 8·55

[a] Composite peak.

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[1] A. DeCian and R. Weiss, *Chem. Comm.*, 1968, 348.

[2] K. Ogawa, A. Torii, H. Kobayashi-Tamura, T. Watanabé, T. Yoshida, and S. Otsuka, *Chem. Comm.*, 1971, 991.

[3] S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1969, **8**, 2514.

[4] M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.*, **5**, 225 (1967).

[5] M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1687.

[6] C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 1959, 3728; M. Corbett and B. F. Hoskins, *Chem. Comm.*, 1968, 1602.

[7] G. D. Meakins and R. J. Moss, *J. Chem. Soc.*, 1957, 993.

[8] R. A. Walton, *Quart. Rev.*, 1965, **19**, 126.

suggests that the two unidentate carbodi-imide ligands are *trans* in the solid state.[9] The ^{1}H n.m.r. spectra the di-t-butylcarbodi-imide complexes are complicated by extensive dissociation in C_6H_6 and $CDCl_3$ solutions to give, on the basis of similar dissociation observed[10] in $(PhCN)_2PdX_2$ systems, a halogen-bridged dimeric species $[LPdX_2]_2$ and free ligand. In benzene solution, five resonances are observed and are assigned to the two non-equivalent t-butyl groups in *trans*-L_2PdX_2, the two non-equivalent t-butyl groups in the bridged system $[LPdX_2]_2$, and to the free ligand. In $CDCl_3$, overlap of the resonances of the monomer and dimer occurred, but these were sufficiently well separated from the Bu^t resonance of the free ligand to allow calculation of the degree of dissociation [*e.g.* 0·31 for a 0·010 molal solution of $(Bu^tN{:}C{:}NBu^t)_2PdCl_2$] of the complex. Under comparable conditions, the apparent molecular weight (370), calculated on this basis for $(Bu^tN{:}C{:}NBu^t)_2PdCl_2$, corresponded, within experimental error, to that observed in the osmometric measurement in $CHCl_3$ (found, 400; calculated 490). The extent of dissociation of the corresponding bromide complex was greater but no dissociation was detected in the methyl-t-butylcarbodi-imide complexes. For these compounds however, very weak resonances were reproducibly observed slightly to low field of the methyl and t-butyl resonances, in an approximate ratio 1 : 3, and are tentatively assigned to another isomeric form of the molecules. The spectroscopic measurements do not indicate the point of co-ordination in the methyl-t-butylcarbodi-imide compounds. On steric grounds, co-ordination through the methyl–nitrogen would seem to be favoured, but, if this is so, the reason for lack of sensitivity of the chemical shift of the methyl protons to complexation, and the small, but significant, shift to low field of the Bu^t-protons is not clear.

As expected for nitrogen donor complexes of the type L_2PdX_2, triphenylphosphine readily displaced the carbodi-imide ligand from $(MeN{=}C{=}NBu^t)_2PdCl_2$ and $(Bu^tN{=}C{=}NBu^t)_2PdCl_2$ in $CHCl_3$ solutions to give almost quantitative yields of *trans*-$(Ph_3P)_2PdCl_2$ which was identified spectroscopically and from its melting point, by comparison with an authentic sample.

Despite the fact that alcohols are known[11] to be unreactive towards carbodi-imides at room temperature, bis(isourea) complexes of stoicheiometry $[RNH{\cdot}C(OCH_3){:}NR']_2PdX_2$ (where X = Cl and Br) were obtained in the reactions between methyl-t-butyl-, di-*o*-tolyl-, and dicyclohexylcarbodi-imides and either Na_2PdX_4 or $(PhCN)_2PdX_2$ in methanol.

Identical compounds were prepared directly from the appropriate isourea and Na_2PdX_4. The 1,2-addition reaction of methanol to the carbodi-imide has clearly been activated by Pd^{II} in these cases, but did not occur for di-t-butylcarbodi-imide which gave the previously discussed bis(carbodi-imide) complex. The failure of Pd^{II} to promote this addition is consistent with the observed failure of Cu_2Cl_2 to catalyse the reaction[12] and is possibly due to the adverse steric effects of the t-butyl groups. Tertiary alkyl groups also inhibit polymerization reactions (1,2-self-additions) of carbodi-imides.[13] A mechanism for the catalysis by trace amounts of Cu^I (ref. 12) and Cu^{II} (ref. 14) salts has been proposed, by analogy with that for the reaction of carbodi-imides with Grignard reagents, and involves the intermediacy of a chloroformamidine–copper species, $RN(Cu){\cdot}CCl{:}NR'$. An insertion of this type was considered earlier as a possible mode of reaction of a carbodi-imide with a Pd–X bond, but, in CH_2Cl_2 solution at least, did not take place. For the Pd^{II} systems, co-ordination through one nitrogen lone pair may sufficiently activate the ligand toward the addition reaction. The ready reaction of $(MeN{:}C{:}NBu^t)_2PdCl_2$ with methanol to give the isourea complex supports this. The isourea complexes are monomeric, non-ionic, and diamagnetic compounds, yellow for X = Cl, and yellow-orange for X = Br. Spectroscopic observations (infrared, Table 3; ^{1}H n.m.r. Table 4) generally support their formulation as *trans*-L_2PdX_2 systems, but show puzzling features for the di-*o*-tolyl and methyl-t-butyl compounds.

TABLE 3

Selected i.r. data (cm^{-1}) for isoureas and isourea complexes

Compound	νNH [a]	νC=N [a]	νC–N [b]	νPd–X [a]
$C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}$	3444m	1665s	1320s	
$[C_6H_{11}{\cdot}C(OCH_3){:}NC_6H_{11}]_2$-$PdCl_2$	3340m	1625s	1356s	338m
$[C_6H_{11}{\cdot}NH{\cdot}C(OCH_3){:}NC_6$-$H_{11}]_2PdBr_2$	3335m	1618m	1360s	266m
o-$CH_3C_6H_4NH{\cdot}C(OCH_3){:}$-N-*o*-$CH_3C_6H_4$	3420m	1664s	1348s	
[*o*-$CH_3C_6H_4NH{\cdot}C(OCH_3){:}$-N-*o*-$CH_3C_6H_4]_2PdCl_2$	3300m	1615vs, 1588s	1385s	323m
[*o*-$CH_3C_6H_4NH{\cdot}C(OCH_3){:}$-N-*o*-$CH_3C_6H_4]_2PdBr_2$	3380m	1610vs, 1590s	1376s	257m
$MeNH{\cdot}C(OCH_3){:}NBu^t$	3445m sh; 3360m br [c]	1660s	1340s	
$[MeNH{\cdot}C(OCH_3){:}NBu^t]_2$-$PdCl_2$	3358m	1626s	1374s 1358s	364m 325m 311m
$[MeNH{\cdot}C(OCH_3){:}NBu^t]_2$-$PdBr_2$	3362m	1620s	1380s 1374s	244m

[a] Nujol mulls. [b] Hexachlorobutadiene mulls. [c] Effect of hydrogen bonding in ligand (see ref. 15).

In each case the characteristic[15] C=N stretching absorption of the isourea was shifted significantly to lower energy on co-ordination but the C–N absorption moved to higher energy. The ν_{N-H} absorption was shifted substantially (generally *ca.* 100 cm^{-1}) to lower

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[9] D. M. Adams, 'Metal-Ligand and Related Vibrations,' Edward Arnold, London, 1967.

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[11] H. Ulrich, 'Cycloaddition Reactions of Heterocumulenes' Academic Press, New York, 1967.

[12] E. Schmidt and F. Moosmüller, *Annalen*, 1955, **597**, 235.

[13] G. C. Robinson, *J. Polymer Sci.*, Part A, 1964, **2**, 3902.

[14] E. Schmidt and W. Carl, *Annalen*, 1961, **639**, 24.

[15] S. E. Forman, C. A. Erickson, and H. Adelman, *J. Org. Chem.*, 1963, **28**, 2653.

energy. These observations suggest that the NH nitrogen is co-ordinated to the palladium. However molecular models of the complexes suggest that, while severe steric interactions exist in both forms, co-ordination through the imine nitrogen is preferred. *X*-Ray crystallographic studies show that the acetamidine molecule in diamine-bis(acetamidine)platinum(II) chloride monohydrate is bound to the metal through the imine nitrogen.[16] On this basis, the reason for the lowering of ν_{N-H} is unclear but may simply reflect severe non-bonded interactions in the molecule. Two $\nu_{C=N}$ absorptions were observed for the di-*o*-tolylisourea complexes and suggest the existence of two isomeric forms in the solid state. However only one ν_{Pd-X} absorption was detected for these and the dicyclohexyl complexes, consistent with only a *trans*-L_2PdX_2 geometry. The isomers probably arise from isomerism within the ligand. In the case of the methyl-t-butylisourea complexes, two ν_{C-N} absorptions and, for X = Cl, three absorptions (364, 325, and 311 cm^{-1}) in the ν_{Pd-Cl} region were observed. The isomerism here is probably *cis–trans* in the square-planar system and the 364 cm^{-1}, and 325 and 311 cm^{-1} absorptions are tentatively assigned to the *trans*- and *cis*-species respectively.

TABLE 4

^{1}H N.m.r. data for isoureas and their complexes (in $CDCl_3$ relative to internal Me_4Si)

Compound	τNH	τOCH_3	τN–CH	τ(*o*–CH_3)	τCH_3	τBu^t
$C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}$	[a]	6·36	6·49			
			7·16			
$[C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}]_2PdCl_2$	3·54	6·04	6·74			
			6·90			
$[C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}]_2PdBr_2$	3·72	6·12	6·72			
			6·96			
o-$CH_3C_6H_4NH{\cdot}C(OCH_3){:}N$-*o*-$CH_3C_6H_4$	4·49	6·07		7·77		
				7·95		
[*o*-$CH_3C_6H_4NH{\cdot}C(OCH_3){:}N$-*o*-$CH_3C_6H_4]_2PdCl_2$	1·12	6·58		7·60		
	4·06	4·86		7·72		
				7·96		
[*o*-$CH_3C_6H_4NH{\cdot}C(OCH_3){:}N$-*o*-$CH_3C_6H_4]_2PdBr_2$	1·44	6·44		7·64		
	4·16	5·02		7·80		
				7·86		
$MeNH{\cdot}C(OCH_3){:}NBu^t$	6·01 [b]	6·30			7·26	8·60
$[MeNH{\cdot}C(OCH_3){:}NBu^t]_2PdCl_2$	3·49	5·11			7·13	8·67
	5·77	6·28				
$[MeNH{\cdot}C(OCH_3){:}NBu^t]_2PdBr_2$	3·76	5·18			7·17	8·73
	5·82	6·30				8·63

[a] Not observed. [b] Neat liquid.

The ^{1}H n.m.r. spectra of the di-cyclohexylisourea complexes in $CDCl_3$ solution are consistent with a single species of this formulation, but the spectra of the di-*o*-tolyl and methyl-t-butyl compounds are complex. Assignments for the di-*o*-tolylisourea compounds in $CDCl_3$ were made by analogy with the free-ligand spectra and by integration, and show that two isomers (in approximate ratio 2 : 1) are present. For X = Br, a weak methoxy-resonance corresponding in position to that of the free ligand is observed, which suggests that the solution behaviour may be further complicated by dissociation of the type discussed for $(Bu^tN{:}C{:}NBu^t)_2PdX_2$. The chemical shifts of the NH protons in the two isomers differed widely from one another as did the methoxy-resonances. The reason for this is unknown but models of possible molecules suggested that severe non-bonded interactions are present in each case. Only in the less-abundant isomer were the resonances of the two non-equivalent *o*-tolyl groups separated. A final feature of the ^{1}H n.m.r. spectra, again indicative of severe crowding in the molecule, was the observation of two barely resolved broad resonances about 1 p.p.m. below the complex aromatic peaks and comprising about one eighth of their intensity. These are tentatively assigned to one set of *ortho*-protons in the co-ordinated isourea molecules.

Two solution forms of the methyl-t-butylisourea compounds were also observed, in approximate ratios 1 : 1 for X = Cl and 2 : 1 for X = Br. Again there were large differences between the chemical shifts of the two NH resonances, and also the OCH_3 resonances, and for X = Br a small separation in the Bu^t signals. Possible isomerism, arising from the direction of addition of methanol to the carbodi-imide, further complicates the interpretation of this system. The ^{1}H n.m.r. spectrum of the uncomplexed ligand contains only one set of resonances which measurements of $J(^{13}C-^1H)$ coupling constants suggest can be assigned to the structure $MeNH{\cdot}C(OMe){:}NBu^t$. The coupling constant in the MeN resonance (132 ± 0·5 Hz) corresponds closely to those observed[17] in a variety of MeNH systems (130—132 Hz) and is significantly lower than the values for MeN: units (*e.g.* $MeN{:}C{:}NBu^t$, $J = 139 \pm 0{\cdot}5$ Hz). This structural conclusion cannot, however, be extended safely to the complexes, for which no measurement of coupling constants has yet been possible, since rapid interconversion of the two tautomeric forms, as

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[16] N. C. Stephenson, *J. Inorg. Nuclear Chem.*, 1963, **24**, 803.

[17] N. S. Ham, personal communication.

has been invoked[18] to explain chemical properties of *NN'*-substituted amidines, or permanent rearrangement of the ligand, may occur.

Triphenylphosphine displaced the isourea from dichlorobis(dicyclohexylisourea)palladium(II) in $\mathrm{CHCl_3}$ to give an almost quantitative yield of *trans*-$\mathrm{(Ph_3P)_2PdCl_2}$. Although deprotonation of the co-ordinated isourea could be a route to complexes of stoicheiometry $\mathrm{[(L{-}H)_2Pd]_2}$, in which the deprotonated isourea (L–H) could function as a bridging bidentate ligand, preliminary studies have led only to decomposition of the complex with the formation of metallic palladium.

EXPERIMENTAL

Elemental analyses and molecular-weight measurements (Table 5) were performed by the Australian Microanalytical Service, C.S.I.R.O., or by Mr. J. Kent of this Department.

TABLE 5

Elemental analyses, molecular weights and melting points for $\mathrm{L_2PdX_2}$ complexes

L	X	M.p. (°C)	C%	H%	N%	X%	*M*
$\mathrm{MeN{:}C{:}NBu^t}$	Cl	—	35·3(35·9)	6·1(6·0)	13·6(13·9)	18·0(17·6)	415(401)
$\mathrm{MeN{:}C{:}NBu^t}$	Br	117—119	29·3(29·4)	5·0(4·9)	11·4(11·4)	32·8(32·6)	
$\mathrm{Bu^tN{:}C{:}NBu^t}$	Cl	151—153	44·6(44·5)	7·4(7·5)	11·2(11·5)	14·7(14·6)	401(490)
$\mathrm{Bu^tN{:}C{:}NBu^t}$	Br	123—125	37·2(37·6)	6·3(6·3)	10·0(9·8)	28·0(27·8)	415(575)
$\mathrm{MeNH{\cdot}C(OCH_3){:}NBu^t}$	Cl [a]	—	35·3(36·1)	6·8(6·9)	11·7(12·0)		499(466)
$\mathrm{MeNH{\cdot}C(OCH_3){:}NBu^t}$	Cl [b]	176—177d	35·7(36·1)	6·9(6·9)	11·8(12·0)	15·4(15·2)	
$\mathrm{MeNH{\cdot}C(OCH_3){:}NBu^t}$	Br [b]	166—167d	30·6(30·3)	6·0(5·8)	9·9(10·0)	28·7(28·8)	590(554)
$\mathrm{C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}}$	Cl [a]	150d	51·6(51·4)	8·2(8·0)	8·3(8·6)	11·2(10·8)	640(654)
$\mathrm{C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}}$	Cl [b]	—	51·2(51·4)	8·1(8·0)	8·4(8·6)	11·1(10·8)	
$\mathrm{C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}}$	Br [a]	—	44·8(45·3)	7·1(7·1)	7·5(7·5)	22·8(21·5)	
$\mathrm{C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}}$	Br [b]	180d	45·1(45·3)	7·2(7·1)	7·1(7·5)	22·5(21·5)	
o-$\mathrm{CH_3C_6H_4NH{\cdot}C(OCH_3){:}N}$-*o*-$\mathrm{CH_3C_6H_4}$	Cl [a]	—	55·6(56·0)	5·4(5·3)	8·2(8·2)	10·6(10·3)	730(686)
o-$\mathrm{CH_3C_6H_4NH{\cdot}C(OCH_3){:}N}$-*o*-$\mathrm{CH_3C_6H_4}$	Cl [b]	180d	56·0(56·0)	5·4(5·3)	8·2(8·2)	10·3(10·3)	
o-$\mathrm{CH_3C_6H_4NH{\cdot}C(OCH_3){:}N}$-*o*-$\mathrm{CH_3C_6H_4}$	Br [b]	180d	49·7(49·6)	4·8(4·7)	6·8(7·2)	20·6(20·6)	

[a] From carbodi-imide. [b] From isourea.

(Calculated values in parentheses)

Infrared spectra were recorded on a PE225 spectrophotometer and ^{1}H n.m.r. spectra on a Jeolco Minimar MH100 spectrometer. Molar conductances were measured in nitrobenzene at room temperature, and magnetic susceptibilities on powdered samples, also at room temperature, using the Gouy method.

Commercial samples of di-*o*-tolylcarbodi-imide (Aldrich) and dicyclohexylcarbodi-imide (B.D.H.) were used without further purification. The following known compounds, for which satisfactory elemental analyses were obtained, were prepared by established methods, and purified by fractional distillation under the conditions listed:

$\mathrm{MeN{:}C{:}NBu^t}$ (124—126°/754 mm; lit.,[19] 121—123°/723 mm); $\mathrm{Bu^tN{:}C{:}NBu^t}$ (48·5—49·5 °C/10 mm; lit.,[19] 47·5—48·5/10 mm); *o*-$\mathrm{CH_3C_6H_4NH{\cdot}C(OCH_3){:}N}$-*o*-$\mathrm{CH_3C_6H_4}$ (140 °C/0·5 mm); $\mathrm{C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}}$ (106—108 °C/1 mm; lit.,[14] 162—163°/11 mm); $\mathrm{MeNH{\cdot}C(OCH_3){:}NBu^t}$ (51—53 °C/11 mm; lit.,[14] 51—53·5°/11 mm).

Preparation of Carbodi-imide Complexes.—(i) *In methylene dichloride*. The preparation of dichlorobis(di-t-butylcarbodi-imide)palladium(II) is representative.

Di-t-butylcarbodi-imide (0·7 g, 4·5 mmol) was stirred with a suspension of $\mathrm{(PhCN)_2PdCl_2}$ (0·75 g, 2·0 mmol) in methylene dichloride (10 ml). The solution quickly cleared and became deep yellow. After 1 h hexane (10 ml) was added and the solution cooled. The yellow crystals formed were filtered off, recrystallized from methylene dichloride–hexane, and dried (50 °C/0·1 mm); yield, 0·7 g (55%).

Dibromobis(di-t-butylcarbodi-imide)palladium(II) (yield, 41%), dichlorobis(methyl-t-butylcarbodi-imide)palladium(II) (yield, 82%), and dibromobis(methyl-t-butylcarbodi-imide)palladium(II) (yield 59%) were prepared similarly.

(ii) *In methanol*. Di-t-butylcarbodi-imide (1·0 g, 6·5 mmol) was stirred with a solution of $\mathrm{Na_2PdCl_4}$ (0·8 g, 2·7 mmol) in dry methanol (50 ml) for 2 h. Concentration of the solution and cooling gave yellow crystals which were filtered off, recrystallized from methylene dichloride–hexane, and dried; yield 0·6 g, 46%.

Preparation of Isourea Complexes.—(i) *From* $\mathrm{PdX_4^{2-}}$ *and carbodi-imides in methanol*. The following preparation is representative. Dicyclohexylcarbodi-imide (1·2 g, 5·8 mmol) was stirred with a solution of $\mathrm{Na_2PdCl_4}$ (0·8 g, 2·7 mmol) in dry methanol (80 ml). The initial red colour of the solution was discharged in a few minutes and a yellow solid was precipitated. The solid was filtered off, recrystallized from methylene dichloride–hexane, and dried to give 0·7 g (40% yield) of dichlorobis(1-cyclohexyl-2-methyl-3-cyclohexylisourea)palladium(II).

Dibromobis(1-cyclohexyl-2-methyl-3-cyclohexylisourea)-palladium(II) (37% yield), dichlorobis(1-*o*-tolyl-2-methyl-3-*o*-tolylisourea)palladium(II) (60% yield), and dichlorobis(1,2-dimethyl-3-t-butylisourea)palladium(II) (60% yield) were prepared similarly.

(ii) *From* $\mathrm{PdX_4^{2-}}$ *and isoureas in methanol*. The dicyclohexylisourea, $\mathrm{C_6H_{11}N{\cdot}C(OCH_3){:}NC_6H_{11}}$, (1·50 g, 6·3 mmol) was stirred with a solution of $\mathrm{Na_2PdCl_4}$ (0·84 g, 2·7 mmol) in dry methanol (30 ml). After 5 min, precipitation of a yellow solid commenced. The solid was filtered off after 5 h and recrystallized (methylene dichloride–hexane) to give 1·05 g (57%) of the dicyclohexylisoureapalladium complex.

The following compounds were prepared similarly: $\mathrm{[C_6H_{11}NH{\cdot}C(OCH_3){:}NC_6H_{11}]_2PdBr_2}$ (37%), [*o*-$\mathrm{CH_3C_6H_4}$-$\mathrm{NH{\cdot}C(OCH_3){:}N}$-*o*-$\mathrm{CH_3C_6H_4]_2PdCl_2}$ (90%), [*o*-$\mathrm{CH_3C_6H_4NH{\cdot}C(OCH_3){:}N}$-*o*-$\mathrm{CH_3C_6H_4]_2PdBr_2}$ (89%), $\mathrm{[MeNH{\cdot}C(OCH_3){:}N\text{-}Bu^t]_2PdCl_2}$ (76%), and $\mathrm{[MeNH{\cdot}C(OCH_3){:}NBu^t]_2PdBr_2}$ (77%).

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