Organometallics 1987, *6*, 1553-1560

Bis-Ortho-Metalated Palladium Complexes. New Examples and Reactivity. The X-ray Crystal Structure of *cis*-$(2\text{-}C_6H_5N{=}NC_6H_4)_2Pd$ and *cis*-$(2\text{-}C_6H_5N{=}NC_6H_4)(2\text{-}Me_2NCH_2C_6H_4)Pd$

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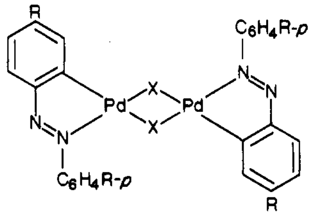
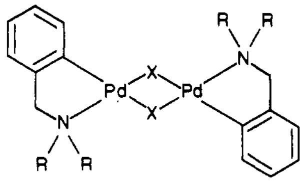
Reaction of bis[(2-(arylazo)aryl)chloropalladium] with 2-lithio-*N*,*N*-dimethylbenzylamine yields the "mixed" ortho-metalated *cis*-[(2-arylazo)aryl)(2-((dimethylamino)methyl)phenyl]palladium], together with both bis(2-(arylazo)aryl)palladium and bis(2-((dimethylamino)methyl)phenyl)palladium. The X-ray structures of *cis*-[(bis(2-phenylazo)phenyl)palladium] and of *cis*-[(2-((dimethylamino)methyl)phenyl)-(2-(phenylazo)phenyl)palladium] have been determined and compared with those of known related molecules. The ((arylazo)aryl)palladium complexes fail to insert alkenes. Bis(2-((dimethylamino)methyl)phenyl]-palladium is shown to insert both styrene and carbon monoxide, and the efficient insertion of methyl acrylate into bis[(2-((*tert*-butylimino)methyl)phenyl)chloropalladium] is also described. β-Elimination following insertion leads to the palladium-free product in each case.

Introduction

The facile ortho-metalation by palladium and platinum halides of azobenzene[1] and of *N*,*N*-dialkylbenzylamines[2] was first described by A. C. Cope and his co-workers. The resultant dimeric halogen-bridged complexes 1 and 2 and especially the chlorides of the latter type have been the subjects of numerous studies, as have analogues with related ligands, with donor atoms other than nitrogen, and a wide range of ortho-metalated complexes of many other transition metals.[3]



1a: R = H; X = Cl
b: R = CH_3; X = Cl
c: R = OCH_3; X = Cl
d: R = H; X = $OCOCH_3$
e: Pt for Pd; R = H; X = Cl



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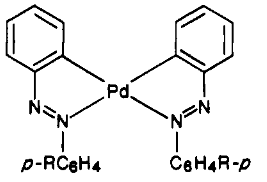
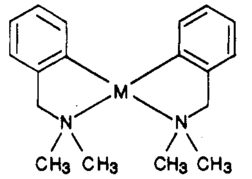


3a: R = H
b: R = CH_3
c: R = OCH_3



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Complexes in which the metal is surrounded by two (or three) such chelating aryl ligands have been examined much less extensively. The palladium complexes **3b**,**c** of azoarenes were first described by one of us,[4] and the analogous complex of *N*,*N*-dimethylbenzylamine 4 (M = Pd) has been synthesized in several ways.[5-7] We also prepared[8] hexacoordinate rhodium complexes of the type **5**. Our continuing interest in such compounds was aroused in part by the observation[8] that one of these rhodium complexes on treatment with carbon monoxide underwent aryl coupling to yield 2,2′-bis(phenylazo)biphenyl (**6**) in contrast to the smooth carbonylation of complex **1a** which yielded 2-phenylindazolone. We believe that this behavior is associated with the cis relationship of the two metal–carbon bonds, but this postulate is difficult to verify in the absence of the corresponding trans isomer. Indeed throughout this field there appear to be few well-authenticated cis/trans pairs. Three platinum complexes were the only examples known in both forms when the present work was initiated: *cis*-bis(2-((diethylamino)methyl)phenyl)- and *cis*-bis(2-((dimethylamino)methyl)phenyl)platinum and the corresponding trans isomers had been described.[6] The latter are the less stable and convert to the cis compounds at 150 °C.[7] The oxygen chelate **7**, which is slowly converted from the white trans to the more stable yellow cis isomer even at room temperature,[9] is not strictly comparable, having only one chelated 8-methoxynaphthyl ligand. Many related compounds have been formulated as cis isomers but frequently without adequate evidence or even without discussion. Our original description[4] of complex **3b** unfortunately gave an erroneous melting point, and the observation of a different value led Sokolov, Troitskaya, and Reutov[10] to surmise that they had obtained the other (probably trans) stereoisomer by a different synthetic route. Reexamination of our old sample

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[1] Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.

[2] Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

[3] For reviews see: Ryabov, A. D. *Synthesis* **1985**, 233. Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. Omae, I. *Chem. Rev.* **1979**, *79*, 287; *Coord. Chem. Rev.* **1979**, *28*, 97; **1980**, *32*, 235; **1982**, *42*, 245.

[4] Bagga, M. M.; Flannigan, W. T.; Knox, G. R.; Pauson, P. L. *J. Chem. Soc. C* **1969**, 1534.

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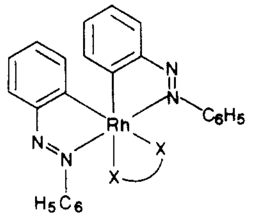
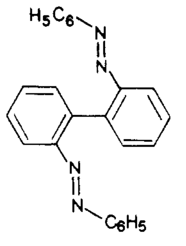
showed that it has the melting point reported by the Russian authors and is undoubtedly identical. The X-ray crystallographic study reported below establishes the cis structure for the parent compound **3a**. On the other hand, cis–trans pairs of palladium compounds have recently been obtained from insertions of hexafluorobutyne-2 into several chelated bis(amine) complexes of palladium.[11] In these reactions the trans isomers are the kinetic products and slowly isomerize to the more stable cis compounds on standing; as in the platinum case the trans isomers tend to be more highly colored (yellow) than the cis forms (colorless or very pale yellow). Two apparently stable trans palladium compounds (**8**, n = 1 or 2) have had their structures established crystallographically.[12,13]

Although we have failed to obtain new cis–trans pairs, we have now obtained the *cis*-azoarene complexes **3** by a third route and synthesized a series of novel (azoarene)(*N*,*N*-dimethylbenzylamine)palladium complexes (**10**) and show by X-ray crytallography of one of these and NMR correlation that these also adopt the cis arrangement of the two chelating C–N ligands. None of the palladium-bonded (arylazo)arene groups appear capable of undergoing insertion reactions while we have shown that bis(2-((dimethylamino)methyl)phenyl)palladium inserts both carbon monoxide and styrene and have also provided new examples of alkene insertion into the related bis[(2-((*tert*-butylimino)methyl)phenyl)chloropalladium].



5a: X⌒X = O_2CCH_3
b: X⌒X = $Cl_2Rh(CO)_2$



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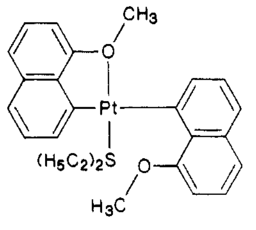

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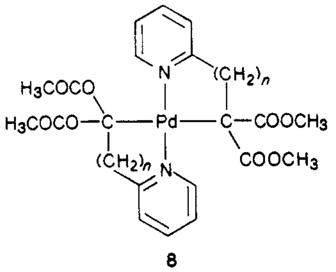

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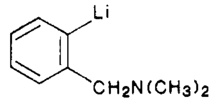

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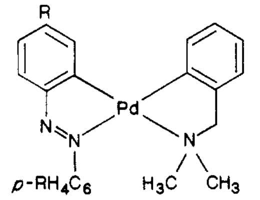


10a: R = H
b: R = CH_3
c: R = OCH_3

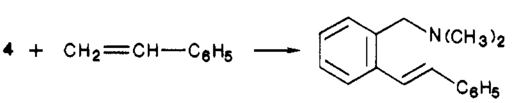
Discussion

One of the routes to the bis(dimethylbenzylamine)-derived chelate of palladium (**4**, M = Pd) is treatment of the dimer **2** (R = Me, X = Cl) with the readily available[14] *o*-lithio-*N*,*N*-dimethylbenzylamine (**9**). With use of other halogen-bridged palladium complexes containing one metalated amine ligand and the same (**9**) or related lithio amines, a number of unsymmetrical bis-metalated palladium chelates have been obtained.[5,14] For our studies of insertion reactions we wished to have such mixed complexes available in which one of the ligands is an *ortho*-metalated azoarene and here describe three examples (**10**, R = H, CH_3, or OCH_3) of this type. They were obtained as the major products by using the same process—i.e., the reaction of the chlorine-bridged complexes **1a–c** with the lithio amine **9**. The latter was always used in excess in order to maximize the yield of the mixed product **10**. When a 2:1 molar ratio of lithio amine to palladium complex was used, the symmetrical bis(arylazo) complexes **3** were also formed in significant amounts. As the ratio was further increased (up to 5:1), the yield of mixed complex improved somewhat and that of the bis(arylazo) compounds decreased; significant amounts of the bis(amine) complex **4** (M = Pd) were formed at these higher ratios. The French workers[11] had also observed symmetric byproducts by using this route without effecting separation from the major mixed products.

^{13}C NMR spectra for the bis-chelated complexes **3a**, **10a**, and **10c** are presented in Table I and compared with published data for complexes **4**. They show that the values for a given ligand are almost independent of the second ligand and are unaffected by the change from platinum to palladium in the series of cis complexes [there is somewhat greater divergence between cis and trans isomers of complex **4** (M = Pt)].

The X-ray crystal structure of the mixed azobenzene–dimethylbenzylamine complex **10a** is described below and compared with that of the bis(azobenzene) complex **3a** and with other related compounds. Like these it adopts the cis configuration (with respect to the Pd–C or Pd–N bonds).

Some new insertion reactions have been observed in the course of our work. Like the chloro-bridged complex **2** (R = CH_3, X = Cl),[15] (bis((dimethylamino)methyl)phenyl)palladium (**4**, M = Pd) inserts styrene when warmed with this alkene in the presence of acetic acid; as usual, β-elimination follows such insertion leading to the metal-free product, here 2-((dimethylamino)methyl)stilbene.



(1)

Neither this nor an azobenzene insertion product could be detected when the mixed complex **10a** was treated similarly; dimethylbenzylamine was liberated under these conditions while most of the azobenzene remained complexed to palladium, the acetoxy-bridged complex **1d** being isolated in 69% yield. Separate experiments showed that neither the corresponding chloride **1a** nor related monomeric (azobenzene)palladium complexes, e.g., $(C_6H_5N{=}NC_6H_4)Pd(PPh_3)Cl$, insert styrene.

Longoni et al.[6] described insertion of carbon monoxide into the σ-Pt–C bond of *trans*-bis((diethylamino)methyl)phenyl)platinum to yield an acylplatinum complex but apparently observed no insertion into the cis isomer. We have treated the cis palladium complex **4** (M = Pd) under similarly mild conditions (room temperature; 1 atm)

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(11) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.

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(13) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Fronczek, F. R. *Organometallics* **1983**, *2*, 1247.

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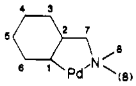
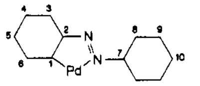
Table I. ^{13}C NMR Data (δ in $CDCl_3$) for Dimethylbenzylamine Complexes



compd	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
trans-4 (M = Pt)[a]	169.4	149.3	120.8	122.4	124.9	134.8	80.2	53.5
$J(^{195}Pt-^{13}C)$	740		19.4		32.4	38.8	18.5	
cis-4 (M = Pt)[a]	138.7	147.3	121.1	122.2	125.7	138.8	73.6	50.0
$J(^{195}Pt-^{13}C)$	1165		39.8	8.3	86.0	109.1	57.3	
cis-4 (M = Pd)[b]	155.9	147.2	121.7	122.8	126.0	139.8	72.2	49.2
10a[c]	156.4	148.1	(122.2	124.2	126.4)	(138.2)	72.6	48.8
10c[c]	(158.2)	148.2	(122.2	124.0	132.35)	137.6	72.9	49.0



	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
3a	157.4	165.55	(125.85	130.75	132.4)	137.0	151.5	121.8	128.1	129.6
10a	157.4	164.6	(124.6	131.1	132.35)	(137.8)	154.3	121.1	129.2	129.0
10c[d]	(159.1)	(159.6)	132.5	110.3	162.2	123.1	148.0	122.7	114.2	160.0

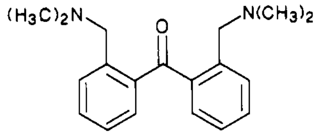
[a] Cf. van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014. [b] Cf. ref 7. [c] This work (assignments in parentheses are tentative). [d] CH_3O: δ 55.6 and 55.5.

Table II. Final Coordinates ($\times 10^4$) for 3a with Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Pd(1)	4274 (1)	4648 (1)	1994 (0)
N(2)	3072 (8)	5444 (7)	3296 (4)
N(3)	1853 (8)	4900 (7)	3645 (4)
N(4)	6095 (8)	5890 (6)	1575 (4)
N(5)	7182 (8)	5421 (7)	887 (4)
C(6)	1408 (10)	3970 (9)	3038 (5)
C(7)	2345 (9)	3637 (8)	2185 (5)
C(8)	1659 (10)	2836 (9)	1610 (5)
C(9)	241 (11)	2297 (10)	1902 (7)
C(10)	−563 (11)	2526 (11)	2761 (7)
C(11)	7 (11)	3393 (10)	3348 (6)
C(12)	3602 (11)	6367 (9)	3910 (5)
C(13)	5468 (11)	6072 (9)	3957 (5)
C(14)	6066 (12)	6909 (11)	4552 (5)
C(15)	4766 (15)	8055 (12)	5045 (6)
C(16)	2910 (15)	8376 (12)	4983 (6)
C(17)	2304 (13)	7500 (10)	4417 (6)
C(18)	7033 (10)	4059 (8)	551 (5)
C(19)	5730 (10)	3425 (8)	943 (4)
C(20)	5848 (10)	1988 (8)	624 (5)
C(21)	7170 (12)	1257 (9)	−63 (5)
C(22)	8353 (12)	1956 (9)	−453 (5)
C(23)	8335 (11)	3366 (9)	−149 (5)
C(24)	6215 (9)	7248 (8)	1964 (4)
C(25)	7898 (11)	7410 (10)	2055 (5)
C(26)	7948 (11)	8741 (11)	2460 (6)
C(27)	6342 (12)	9873 (10)	2761 (5)
C(28)	4674 (12)	9701 (9)	2677 (5)
C(29)	4585 (10)	8372 (8)	2292 (5)

and isolated a remarkably hygroscopic oil which we formulate as 2,2′-bis((dimethylamino)methyl)benzophenone (**11**) on the basis of its NMR and mass spectra and the formation of its dimethiodide. Only partial decomposition occurred when the mixed complex **10a** was treated with carbon monoxide at 50 °C.

In attempts to extend such insertion reactions to yield compounds of greater potential use in heterocyclic synthesis, we have also examined insertion reactions into complexes **12** and **13** obtained, respectively, from benzaldoxime[16] and from *N*-*tert*-butylbenzaldimine.[17] The latter has previously been shown[17] to insert both styrene and acrylonitrile. Neither of these addends reacted under similar conditions with the oxime complex **12**. The imine complex **13** efficiently added methyl acrylate to yield the expected product **14** which was not fully characterized but was hydrogenated to the amino ester **15**. When addition was conducted in a mixture of acetic and trifluoroacetic acids, the initial product **14** hydrolyzed to the corresponding aldehyde. Addition of methyl vinyl ketone on the other hand converted complex **13** to 2-acetylindene **16** presumably via the saturated adduct **17**. Dimethyl fumarate did not react.



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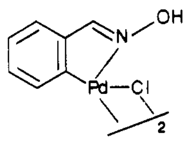

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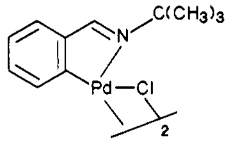

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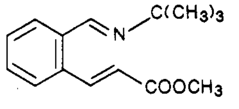

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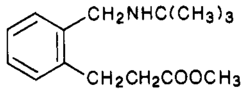

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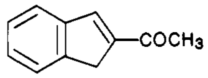

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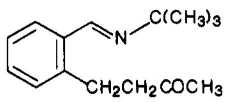

17

Crystal Structures. Single crystal X-ray diffraction studies of bis(2-(phenylazo)phenyl)palladium (**3a**) (by J.A.D.J) and of (2-((dimethylamino)methyl)phenyl)(2-(phenylazo)phenyl)palladium (**10a**) (by K.J.M.) have shown both to have cis structures. Final atomic coordinates, interatomic distances, selected bond angles, nonbonding contacts, and out-of-plane distances are given in Tables II–IV for complex **3a** and in Tables V–VII for complex **10a**. Structure factors and thermal parameters are available as supplementary material. Figure 1 shows the atom numbering for complex **3a**; stereoscopic views of

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(16) Onoue, H.; Minami, K.; Nakegawa, K. *Bull Chem. Soc. Jpn.* **1970**, *43*, 3480.

(17) Girling, J. R.; Widdowson, D. A. *Tetrahedron Lett.* **1982**, *23*, 1957, 4281.

Table III. Selected Valency Parameters for 3a[a]

(a) Bond Lengths (Å)

Pd(1)–N(2)	2.131 (6)	Pd(1)–N(4)	2.133 (6)
Pd(1)–C(7)	2.000 (7)	Pd(1)–C(19)	1.998 (7)
N(2)–N(3)	1.274 (7)	N(4)–N(5)	1.264 (9)
N(2)–C(12)	1.443 (10)	N(4)–C(24)	1.430 (9)
N(3)–C(6)	1.406 (10)	N(5)–C(18)	1.409 (10)
C(6)–C(7)	1.405 (11)	C(18)–C(19)	1.402 (10)
C(6)–C(11)	1.397 (12)	C(18)–C(23)	1.400 (11)
C(7)–C(8)	1.395 (11)	C(19)–C(20)	1.392 (10)
C(8)–C(9)	1.380 (12)	C(20)–C(21)	1.403 (11)
C(9)–C(10)	1.372 (14)	C(21)–C(22)	1.366 (12)
C(10)–C(11)	1.396 (14)	C(22)–C(23)	1.384 (12)
C(12)–C(13)	1.381 (12)	C(24)–C(25)	1.374 (11)
C(12)–C(17)	1.377 (12)	C(24)–C(29)	1.398 (10)
C(13)–C(14)	1.397 (12)	C(25)–C(26)	1.398 (13)
C(14)–C(15)	1.374 (14)	C(26)–C(27)	1.378 (13)
C(15)–C(16)	1.373 (16)	C(27)–C(28)	1.365 (13)
C(16)–C(17)	1.397 (14)	C(28)–C(29)	1.394 (11)

(b) Valency angles (deg)

N(2)–Pd(1)–N(4)	107.5 (2)	C(7)–Pd(1)–C(19)	98.7 (3)
N(2)–Pd(1)–C(7)	78.3 (3)	N(4)–Pd(1)–C(19)	77.8 (3)
N(2)–Pd(1)–C(19)	165.7 (3)	N(4)–Pd(1)–C(7)	169.7 (3)
Pd(1)–N(2)–N(3)	117.1 (5)	Pd(1)–N(4)–N(5)	117.8 (5)
Pd(1)–N(2)–C(12)	129.3 (5)	Pd(1)–N(4)–C(24)	127.9 (4)
N(3)–N(2)–C(12)	113.0 (6)	N(5)–N(4)–C(24)	114.4 (6)
N(2)–N(3)–C(6)	111.6 (6)	N(4)–N(5)–C(18)	111.6 (6)
N(3)–C(6)–C(7)	121.5 (7)	N(5)–C(18)–C(19)	120.9 (7)
N(3)–C(6)–C(11)	115.5 (7)	N(5)–C(18)–C(23)	115.2 (7)
C(7)–C(6)–C(11)	123.0 (7)	C(19)–C(18)–C(23)	123.8 (7)
Pd(1)–C(7)–C(6)	111.2 (5)	Pd(1)–C(19)–C(18)	111.9 (5)
Pd(1)–C(7)–C(8)	132.2 (6)	Pd(1)–C(19)–C(20)	131.5 (5)
C(6)–C(7)–C(8)	116.2 (7)	C(18)–C(19)–C(20)	115.8 (7)
C(7)–C(8)–C(9)	120.9 (7)	C(19)–C(20)–C(21)	121.2 (7)
C(8)–C(9)–C(10)	122.1 (9)	C(20)–C(21)–C(22)	120.7 (8)
C(9)–C(10)–C(11)	119.2 (9)	C(21)–C(22)–C(23)	120.7 (8)
C(6)–C(11)–C(10)	118.3 (8)	C(18)–C(23)–C(22)	117.6 (7)
N(2)–C(12)–C(13)	116.9 (7)	N(4)–C(24)–C(25)	120.8 (6)
N(2)–C(12)–C(17)	121.4 (7)	N(4)–C(24)–C(29)	118.4 (6)
C(13)–C(12)–C(17)	121.7 (8)	C(25)–C(24)–C(29)	120.7 (7)
C(12)–C(13)–C(14)	119.5 (8)	C(24)–C(25)–C(26)	118.7 (8)
C(13)–C(14)–C(15)	118.5 (8)	C(25)–C(26)–C(27)	120.8 (8)
C(14)–C(15)–C(16)	122.0 (10)	C(26)–C(27)–C(28)	120.3 (8)
C(15)–C(16)–C(17)	119.6 (10)	C(27)–C(28)–C(29)	120.2 (8)
C(12)–C(17)–C(16)	118.5 (9)	C(24)–C(29)–C(28)	119.3 (7)

(c) Intermolecular Contacts ⩽ 3.5 Å

contact[b]		type[c]	contact[b]		type[c]
$N(3)\cdots C(14^{I})$	3.35	A···C	$C(14)\cdots N(3^{I})$	3.35	C···A
$N(5)\cdots C(9^{II})$	3.44	A′···B	$C(18)\cdots C(9^{II})$	3.28	B′···B
$C(8)\cdots C(28^{III})$	3.47	B···C′	$C(18)\cdots C(19^{V})$	3.46	B′···B′
$C(9)\cdots N(5^{IV})$	3.44	B···A′	$C(19)\cdots C(18^{V})$	3.46	B′···B′
$C(9)\cdots C(18^{IV})$	3.28	B···B′	$C(23)\cdots C(9^{II})$	3.48	B′···B
$C(9)\cdots C(23^{IV})$	3.48	B···B′	$C(28)\cdots C(8^{VI})$	3.47	C′···B

[a] Estimated standard deviations are given in parentheses. [b] Roman numeral superscripts refer to the following equivalent positions: I, $1 - x$, $1 - y$, $1 - z$; II, $1 + x$, y, z; III, x, -1, $+ y$, z; IV, $-1 + x$, y, z; V, $1 - x$, $1 - y$, $-z$; VI, x, $1 + y$, z. [c] See text.

Table IV. Mean Planes for 3a, Deviations (Å × 10^2) of Atoms from Mean Planes,[a] and Interplanar Angles (deg)

(a) Departures from Planes

plane 1, rings (A + A′):	Pd(1), 3; N(2), –20; C(7), 21; N(4), 18; C(19), –23; *N(3)*, –23; *C(6)*, 4; *N(5)*, 11; *C(12)*, –51; *C(24)*, 41
plane 2, ring B:	C(6), 3; C(7), –4; C(8), 1; C(9), 2; C(10), –2; C(11), 0; *Pd(1)*, 2; *N(3)*, 12
plane 3, ring B′:	C(18), –2; C(19), 2; C(20), 0; C(21), –2; C(22), 2; C(23), 0; *Pd(1)*, –19; *N(5)*, –15
plane 4, ring C:	C(12), 0; C(13), 2; C(14), –1; C(15), 0; C(16), 1; C(17), –1, *N(2)*, 0
plane 5, ring C′:	C(24), 1; C(25) 0; C(26), –1; C(27), 0; C(28), 1; C(29), –1, *N(4)*, –2

(b) Interplanar Angles (deg)

(A + A′)–B	15	B–C	45	B–B′	32
(A + A′)–B′	17	B–C′	50	C–C′	17
(A + A′)–C	43	B′–C	46		
(A + A′)–C′	42	B′–C′	38		

[a] Italicized atoms were not used to locate the mean planes. [b] Ring labeling as in Figure 1.

Table V. Fractional Coordinates for 10a with Standard Deviations in Parentheses

	x	*y*	*z*
Pd(1)	0.41131 (4)	0.33262 (3)	0.39860 (3)
N(1)	0.2303 (5)	0.3576 (4)	0.4160 (4)
N(2)	0.1980 (5)	0.3092 (4)	0.4809 (4)
N(3)	0.4418 (5)	0.4653 (4)	0.3138 (4)
C(3)	0.4870 (7)	0.1680 (5)	0.5533 (5)
C(4)	0.4613 (8)	0.1105 (6)	0.6261 (5)
C(5)	0.3482 (9)	0.1217 (6)	0.6519 (5)
C(6)	0.2604 (8)	0.1886 (5)	0.6019 (5)
C(1)	0.2888 (7)	0.2424 (4)	0.5280 (4)
C(2)	0.4021 (6)	0.2322 (4)	0.4991 (4)
C(8)	0.0978 (4)	0.5113 (3)	0.41784 (20)
C(9)	0.0116 (4)	0.5800 (3)	0.36779 (20)
C(10)	–0.0311 (4)	0.5636 (3)	0.26670 (20)
C(11)	0.0126 (4)	0.4785 (3)	0.21565 (20)
C(12)	0.0988 (4)	0.4098 (3)	0.26570 (20)
C(7)	0.1414 (4)	0.4262 (3)	0.36679 (20)
C(13)	0.3781 (8)	0.5664 (5)	0.3293 (5)
C(14)	0.4155 (8)	0.4325 (6)	0.2085 (5)
C(15)	0.5764 (7)	0.4872 (5)	0.3514 (5)
C(16)	0.6417 (7)	0.3831 (6)	0.3584 (5)
C(17)	0.5800 (6)	0.2950 (5)	0.3847 (5)
C(18)	0.6359 (7)	0.1963 (6)	0.3842 (5)
C(19)	0.7521 (7)	0.1838 (8)	0.3650 (6)
C(20)	0.8132 (9)	0.2693 (9)	0.3426 (7)
C(21)	0.7595 (8)	0.3681 (8)	0.3384 (6)
Pd(2)	0.13156 (4)	0.16683 (3)	0.07689 (3)
N(4)	0.0240 (5)	0.1107 (4)	0.1686 (4)
N(5)	–0.0828 (5)	0.1466 (4)	0.1598 (4)
N(6)	0.2904 (5)	0.0609 (4)	0.1027 (4)
C(24)	–0.0635 (7)	0.3145 (5)	–0.0351 (5)
C(25)	–0.1788 (8)	0.3587 (6)	–0.0529 (6)
C(26)	–0.2605 (7)	0.3319 (5)	0.0002 (6)
C(27)	–0.2268 (6)	0.2644 (5)	0.0722 (6)
C(22)	–0.1112 (6)	0.2210 (5)	0.0897 (5)
C(23)	–0.0228 (5)	0.2465 (4)	0.0373 (4)
C(24)	–0.0018 (4)	–0.0675 (4)	0.2225 (3)
C(30)	0.0353 (4)	–0.1444 (4)	0.2891 (3)
C(31)	0.1306 (4)	–0.1194 (4)	0.3724 (3)
C(32)	0.1889 (4)	–0.0175 (4)	0.3892 (3)
C(33)	0.1517 (4)	0.0595 (4)	0.5228 (3)
C(28)	0.0564 (4)	0.0343 (4)	0.2393 (3)
C(34)	0.2668 (7)	–0.0492 (4)	0.1260 (5)
C(35)	0.399 (7)	0.1112 (5)	0.1758 (6)
C(36)	0.3169 (6)	0.0543 (5)	0.0045 (5)
C(37)	0.3147 (6)	0.1634 (5)	–0.0309 (5)
C(38)	0.2278 (6)	0.2326 (5)	–0.0039 (4)
C(39)	0.2303 (7)	0.3404 (5)	–0.0291 (5)
C(40)	0.3112 (8)	0.3718 (7)	–0.0829 (6)
C(41)	0.3897 (8)	0.2998 (7)	–0.1132 (7)
C(42)	0.3933 (7)	0.1959 (7)	–0.0852 (6)

3a and **10a** and of the unit-cell contents of **3a** are presented in the supplementary material. Figure 2 shows perspective views (including numbering system) for complex **10a**.

The palladium atom in **3a** shows approximately square-planar coordination (but see below). Corresponding bond parameters for the separate azobenzene residues generally differ by less than 1 esd, and greater differences can be ascribed to the effects of intermolecular forces; thus, considerations of one ligand apply to the other. Figure 1 has a vertical line of symmetry through the palladium atom. The distance from N(2) to this line is about half the van der Waals thickness of a benzene ring, implying that rings C and C′ lie parallel but perpendicular to the mean plane through rings A and A′; however, strictly planar coordination at palladium is not possible, as the distances between C(8) and C(20) and between the hy-

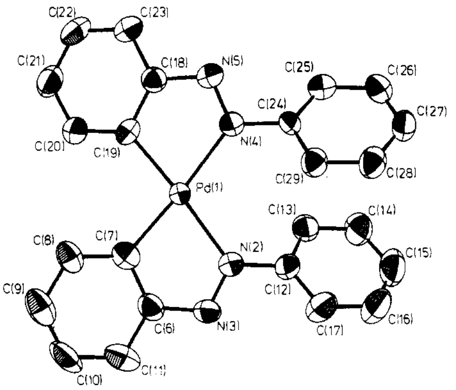

Figure 1. A perspective view (ORTEP[40]) of the molecule of *cis*-bis(2-(phenylazo)phenyl)palladium (**3a**), showing the crystallographic numbering system.

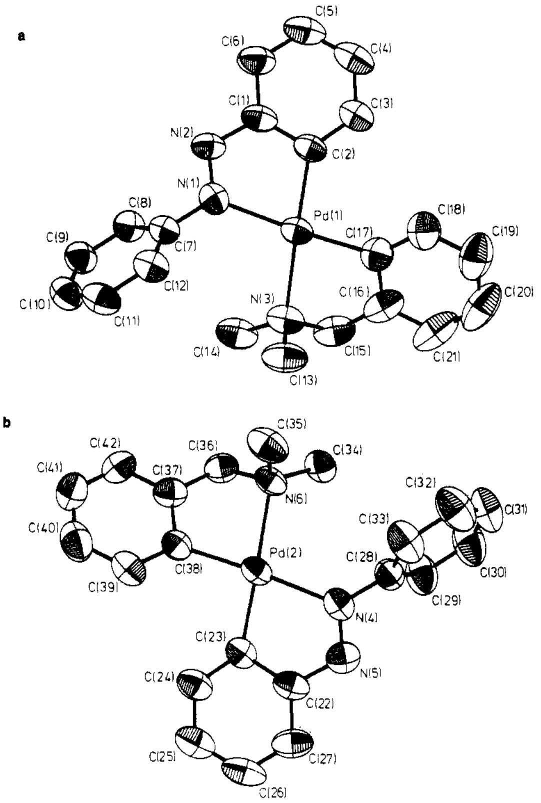

Figure 2. A perspective view (ORTEP[40]) of molecules 1 (a) and 2 (b) of *cis*-bis((2-(dimethylamino)methyl)phenyl)(2-phenylazo)phenyl)palladium (**10a**), showing the numbering system.

drogens attached to these carbon atoms would each be less than the sum of their van der Waals radii. In practice, the bonds at palladium are not coplanar, and rings A and A′ are puckered, moving rings B and B′, one above and one below the plane of Figure 1, relieving their interactions so that the intramolecular separation C(8)···C(20) is 3.294 Å and allowing conrotatory movements of rings C and C′ to occur, about their C–N bonds, until the drive (plausibly for increased conjugation; but see also below) is balanced by van der Waals forces. A more detailed numerical analysis has been deposited. It follows from the analysis of the conformation that the trans analogue of this compound would require excessively close internal contacts of the type B···C′. The intermolecular contacts for the two halves of the molecule differ; N(2) and N(3) are involved in closer contacts than N(4) and N(5). The closest contact involves C(9), which lies near N(2) of one molecule and near C(18) and C(23) of another. If atom labels are replaced by ring labels [for example, any of Pd(1), N(2), N(3), C(6), or C(7) by A], the contacts can be summarized as A···B, A···C, $(B\cdots B')_2$, B′···B′, and B···C′ and their converses (see Table III); rephrased, the packing is dominated by

Table VI. Selected Valency Parameters for 10[a]

(a) Bond Lengths (Å)

Pd(1)–N(1)	2.116 (5)	Pd(2)–N(4)	2.104 (5)
Pd(1)—C(2)	1.992 (6)	Pd(2)–C(23)	1.985 (6)
Pd(1)–N(3)	2.193 (5)	Pd(2)–N(6)	2.198 (5)
Pd(1)–C(17)	1.997 (7)	Pd(2)–C(38)	1.990 (6)
N(1)–N(2)	1.262 (7)	N(4)–N(5)	1.259 (8)
N(1)–C(7)	1.407 (6)	N(4)–C(28)	1.424 (7)
N(2)–C(1)	1.395 (8)	N(5)–C(22)	1.397 (8)
C(1)–C(2)	1.424 (9)	C(22)–C(23)	1.420 (8)
C(1)–C(6)	1.386 (10)	C(22)–C(27)	1.377 (10)
C(2)–C(3)	1.376 (9)	C(23)–C(24)	1.379 (9)
C(3)–C(4)	1.387 (11)	C(24)–C(25)	1.368 (11)
C(4)–C(5)	1.402 (12)	C(25)–C(26)	1.365 (11)
C(5)–C(6)	1.391 (11)	C(26)–C(27)	1.361 (11)
N(3)–C(13)	1.481 (9)	N(6)–C(34)	1.474 (8)
N(3)–C(14)	1.474 (9)	N(6)–C(35)	1.489 (9)
N(3)–C(15)	1.480 (9)	N(6)–C(36)	1.490 (8)
C(15)–C(16)	1.493 (11)	C(36)–C(37)	1.486 (9)
C(16)–C(17)	1.411 (10)	C(37)–C(38)	1.406 (9)
C(17)–C(18)	1.385 (10)	C(38)–C(39)	1.419 (9)
C(18)–C(19)	1.396 (12)	C(39)–C(40)	1.389 (11)
C(19)–C(20)	1.358 (14)	C(40)–C(41)	1.376 (12)
C(20)–C(21)	1.374 (14)	C(41)–C(42)	1.383 (12)
C(21)–C(16)	1.422 (12)	C(42)–C(37)	1.378 (10)

(b) Valency Angles (deg)

N(1)–Pd(1)–N(3)	103.1 (2)	N(4)–Pd(2)–N(6)	103.4 (2)
N(1)–Pd(1)–C(2)	78.5 (2)	N(4)–Pd(2)–C(23)	78.3 (2)
N(1)–Pd(1)–C(17)	174.8 (2)	N(4)–Pd(2)–C(38)	175.0 (2)
N(3)–Pd(1)–C(2)	168.2 (2)	N(6)–Pd(2)–C(23)	170.4 (2)
N(3)–Pd(1)–C(17)	81.9 (2)	N(6)–Pd(2)–C(38)	80.9 (2)
C(2)–Pd(1)–C(17)	97.1 (3)	C(23)–Pd(2)–C(38)	97.9 (2)
Pd(1)–N(1)–N(2)	117.2 (4)	Pd(2)–N(4)–N(5)	117.7 (4)
Pd(1)–N(1)–C(7)	128.1 (3)	Pd(2)–N(4)–C(28)	127.8 (4)
N(2)–N(1)–C(7)	114.7 (5)	N(5)–N(4)–C(28)	114.4 (5)
N(1)–N(2)–C(1)	112.8 (5)	N(4)–N(5)–C(22)	112.7 (5)
Pd(1)–N(3)–C(13)	116.6 (4)	Pd(2)–N(6)–C(34)	116.2 (4)
Pd(1)–N(3)–C(14)	112.4 (4)	Pd(2)–N(6)–C(35)	112.2 (4)
Pd(1)–N(3)–C(15)	101.4 (4)	Pd(2)–N(6)–C(36)	100.5 (4)
C(13)–N(3)–C(14)	109.2 (5)	C(34)–N(6)–C(35)	110.0 (5)
C(13)–N(3)–C(15)	107.8 (5)	C(34)–N(6)–C(36)	108.3 (5)
C(14)–N(3)–C(15)	108.8 (5)	C(35)–N(6)–C(36)	108.9 (5)
N(2)–C(1)–C(2)	120.2 (6)	N(5)–C(22)–C(23)	119.5 (5)
N(2)–C(1)–C(6)	115.8 (6)	N(5)–C(22)–C(27)	117.9 (6)
C(2)–C(1)–C(6)	124.0 (6)	C(23)–C(22)–C(27)	122.5 (6)
Pd(1)–C(2)–C(1)	111.0 (4)	Pd(2)–C(23)–C(22)	111.7 (4)
Pd(1)–C(2)–C(3)	133.1 (5)	Pd(2)–C(23)–C(24)	133.3 (5)
C(1)–C(2)–C(3)	115.2 (6)	C(22)–C(23)–C(24)	114.8 (5)
C(2)–C(3)–C(4)	122.6 (7)	C(23)–C(24)–C(25)	122.5 (7)
C(3)–C(4)–C(5)	120.4 (7)	C(24)–C(25)–C(26)	121.0 (7)
C(4)–C(5)–C(6)	119.4 (7)	C(25)–C(26)–C(27)	119.6 (7)
C(5)–C(6)–C(1)	118.2 (7)	C(26)–C(27)–C(22)	119.6 (7)
N(3)–C(15)–C(16)	109.4 (6)	N(6)–C(36)–C(37)	109.9 (5)
Pd(1)–C(17)–C(16)	111.7 (5)	Pd(2)–C(38)–C(37)	113.3 (4)
Pd(1)–C(17)–C(18)	130.4 (5)	Pd(2)–C(38)–C(39)	129.3 (5)
C(15)–C(16)–C(17)	117.1 (6)	C(36)–C(37)–C(38)	115.4 (6)
C(15)–C(16)–C(21)	123.8 (7)	C(36)–C(37)–C(42)	122.7 (6)
C(17)–C(16)–C(21)	119.1 (7)	C(38)–C(37)–C(42)	121.9 (6)
C(16)–C(17)–C(18)	117.3 (6)	C(37)–C(38)–C(39)	116.9 (6)
C(17)–C(18)–C(19)	122.4 (7)	C(38)–C(39)–C(40)	120.1 (6)
C(18)–C(19)–C(20)	120.2 (8)	C(39)–C(40)–C(41)	121.2 (8)
C(19)–C(20)–C(21)	119.6 (9)	C(40)–C(41)–C(42)	119.7 (8)
C(20)–C(21)–C(16)	121.3 (9)	C(41)–C(42)–C(37)	120.1 (8)

[a] Estimated standard deviations in parentheses.

Table VII. Deviations (Å × 10^2) of Atoms of 10a from Mean Planes through Pd and Its Ligands[a]

molecule 1:	Pd(1), –7; N(1), –11; N(3), 13; C(2), 16; C(17), –11; *N*(*2*), 10; *C*(*1*), 27; *C*(*15*), 93; *C*(*16*), 39
molecule 2:	Pd(2), 5; N(4), 10; N(6), –11; C(23), –13; C(38), 10; *N*(5), 0; *C*(*22*), –12; *C*(36), –94; *C*(37), –42

[a] Italicized atoms were not used to locate the planes.

Table VIII. Bond Lengths (Å) and Torsion Angles (deg) for the Free Phenyl Group in Azobenzene and in 2-(Phenylazo)phenyl Units Bonded (N, C) to a Transition Metal[a]

compd	bond lengths			torsion angle[b]	ref
	(C)C–N	N–N	N–C(B)		
azobenzene	1.428	1.247	1.428	17	31
Rh(O$_2$CMe)(pap)$_2$ (**5a**)	1.42	1.27	1.38	14	35
	1.46	1.29	1.38	22	
(PtClpap)$_2$	1.48	1.23	1.38	39	30
Pd(pap)$_2$ (**3a**)	1.443	1.274	1.406	43	this work
	1.430	1.264	1.409	42	
Ni(cp)(tat)	1.41	1.27	1.35	44	36
Pd(fa)(pap)	1.442	1.281	1.388	46	37
Rh(pap)$_2$(Cl$_2$Rh(CO)$_2$) (**5b**)	1.403	1.311	1.376	45	38
	1.396	1.335	1.383	54	
Pd(pap)(dmp) (**10a**)	1.407	1.262	1.395	66	this work
	1.424	1.259	1.397	70	

[a] Abbreviations: Cp, cyclopentadienyl; dmp, 2-((dimethylamino)methyl)phenyl; fa, 1,1,1,5,5,5-hexafluoroacetylacetonato; pap, 2-(phenylazo)phenyl; tat, 2-((4-tolyl)azo)-4-tolyl. [b] Approximate; see references for different methods of calculation used.

interactions between the B-type rings.

Compound **10a** crystallizes with two molecules in the asymmetric unit; generally, corresponding bond parameters for the two molecules agree within 1 esd of their mean. The conformation of each molecule is determined by constraints similar to those for **3a**. Bonding at palladium is not strictly planar; for the two molecules of one asymmetric unit the systems of ligands at palladium are homochiral.[39] The metalated benzene rings within one molecule are not coplanar, and the separations C(3)···C(18), 3.275 Å, and C(24)···C(39), 3.269 Å, are very similar to the value for **3a**. The ligand in **10a** containing the (dimethylamino)methyl group is more flexible than is an azobenzene system, and the bonding at palladium is more nearly planar in **10a** than in **3a**; however, the departures of the atoms not bonded to palladium, particularly C(15) and C(16), C(36) and C(37) from the plane are greater in **10a** than any such departures for **3a**. The angles between the plane of the phenyl group and the best plane through palladium and its ligand atoms (molecule 1, 66°, molecule 2, 70°) are larger for **10a** than for **3a** (for which the angles are 43° and 42°, respectively), a consequence of the van der Waals radius of a methyl group being greater than the half-thickness of a benzene ring. As for **3a**, the steric requirements for the ligands that comprise **10a** make the existence of the trans analogue very implausible.

For both compounds the Pd–N and Pd–C bonds are mutually trans, and their lengths are similar to those in other molecules with this feature; for example, N–Pd–C, respectively, 2.165 and 2.051 Å;[26] 2.14 and 1.97, 2.15 and 1.99 Å;[27] 2.184 and 2.021 Å;[28] 2.213 and 2.024, 2.234 and 1.990 Å.[29] In **10a** the Pd–N(sp^3) bonds (2.193, 2.198 Å) are longer than the Pd–N(sp^2) bonds (2.116, 2.104 Å). Within the azobenzene residues for both compounds the two C–N bonds differ in length; with use of ring labels (Figure 1) to identify atoms, (C)C–N is longer than N–C(B) in all cases. This difference is common to other azobenzene residues similarly bonded, and the suggestion has been made[30] that interrupted conjugation between ring C and the rest of the π-system is responsible for the greater length of the (C)C–N bond. However, a table of C–N and N–N distances and torsion angles of the (C)C–N bonds (Table VIII) shows no simple correlation between the size of the torsion angle and either absolute bond lengths or the difference between the C–N distances. Generally, the N–N distance is longer than that (1.247 Å) in the better-defined molecule of free azobenzene,[31] but that for **1e** provides an exception; the N–C(B) bond is consistently shorter than in free azobenzene, with values near the mean, 1.385 Å. Other bond parameters for **3a** and **10a** are unexceptional.

Experimental Section

Bis[(2-(arylazo)aryl)chloropalladium]. Our preparation of these complexes is similar to previous methods[1,4,18] except that the reactants were heated for ~1 h at 85–90 °C in aqueous dioxane. Azobenzene (1.04 g, 5.5 mmol) and palladium chloride (0.19 g, 1.1 mmol) were allowed to react in dioxane (50 mL) and water (25 mL), and the product **1a** was collected after cooling, washed with acetone, and dried: yield 0.29 g (84%); mp 280–283 °C dec (lit.[1] mp 279–281 °C dec). Anal. Calcd for $C_{24}H_{18}Cl_2N_4Pd_2$: C, 44.6; H, 2.8; N, 8.7. Found: C, 44.2; H, 2.8; N, 8.6.

4,4′-Dimethylazobenzene (2.94 g, 14 mmol) and palladium chloride (0.5 g, 2.8 mmol) were allowed to react in dioxane (120 mL) and water (25 mL) and the product **1b** filtered from the hot suspension, washed with dioxane and acetone, and dried; yield 0.29 g (93%). Anal. Calcd for $C_{28}H_{26}Cl_2N_4Pd_2$: C, 47.9; H, 3.7; N, 8.0. Found: C, 47.4; H, 3.7; N, 7.9.

4,4′-Dimethoxyazobenzene (3.4 g, 14 mmol) similarly gave the product **1c**, yield 1.07 g (92%). Anal. Calcd for $C_{28}H_{26}Cl_2N_4O_4Pd_2$: C, 43.9; H, 3.4; N, 7.3. Found: C, 44.1; H, 3.4; N, 7.3.

Reactions with 2-Lithio-*N*,*N*-dimethylbenzylamine. (a) Azobenzene Complex 1a. This complex (1 g, 1.55 mmol) was added under nitrogen to a suspension of the lithio compound[14] (0.44 g, 3.10 mmol) in benzene (50 mL). After being stirred at room temperature for 2 h, the solution was concentrated under reduced pressure and the residue chromatographed on alumina. Benzene/petroleum ether (bp 40–60 °C) (1:1) eluted (2-((dimethylamino)methyl)phenyl)(2-(phenylazo)phenyl)palladium (**10a**): orange-red crystals (from dichloromethane/petroleum ether); mp 142–143 °C dec. Anal. Calcd for $C_{21}H_{21}N_3Pd$: C, 59.8; H, 5.0; N, 10.0. Found: C, 59.6; H, 4.9; N, 10.0.

Further elution with the same solvent yielded bis(2-(phenylazo)phenyl)palladium (**3a**) (0.21 g, 29%), mp 161–162 °C dec (lit.[10] mp 163–164.5 °C dec). Anal. Calcd for $C_{24}H_{18}N_4Pd$: C, 61.5; H, 3.9; N, 11.95. Found: C, 61.1, 61.5; H, 3.8, 3.85; N, 11.9, 11.95.

Increased excess of the lithio compound increased the proportion of "mixed" product; thus with lithio compound and azobenzene complex **1a** in a 5:1 ratio, the products **10a** and **3a** were isolated in yields of 53 and 11%, respectively.

In a further experiment employing 2-lithio-*N*,*N*-dimethylbenzylamine (1.76 g, 12.4 mmol) and the palladium complex **1a** (2.0 g, 3.1 mmol) in benzene (100 mL), the products **10a** (0.81 g, 31%) and **3a** (0.13 g, 4.5%) [eluted in the reverse order by benzene/petroleum ether (1:1)] were accompanied by bis(2-((dimethylamino)methyl)phenyl)palladium (**4**, M = Pd) (0.52 g, 22%) which was eluted with chloroform and crystallized from THF, mp 218–220 °C dec (lit.[19] mp 221 °C dec).

(b) Azotoluene Complex 1b. This complex (1.0 g, 1.42 mmol) and 2-lithio-*N*,*N*-dimethylbenzylamine (0.40 g, 2.85 mmol) in benzene (50 mL) similarly yielded, on elution of the chromatogram with benzene/petroleum ether (bp 40–60 °C), first, (2-((dimethylamino)methyl)phenyl)(2-((4-methylphenyl)azo)-5-methylphenyl)palladium (**10b**) (0.46 g, 36%): orange-red crystals (from dichloromethane/petroleum ether); mp 170–171 °C dec. Anal. Calcd for $C_{23}H_{25}N_3Pd$: C, 61.4; H, 5.6; N, 9.3. Found: C, 61.55; H, 5.7; N, 9.45.

This was followed by bis(2-((4-methylphenyl)azo)-5-methylphenyl)palladium (**3b**): orange-red crystals (from dichloromethane/petroleum ether) (0.18 g, 24%); mp 174–175 °C dec (lit.[10] mp 172–176 °C); identical in melting point and IR spectrum with a sample prepared by M. M. Bagga.[4] Anal. Calcd for $C_{28}H_{26}N_4Pd$: C, 64.1; H, 5.0; N, 10.7. Found: C, 64.0; H, 4.9; N. 10.8.

(c) Azoanisole Complex 1c. This complex (1.0 g, 1.3 mmol) and the lithio compound (0.37 g, 1.61 mmol) in benzene (50 mL) similarly gave, on elution with dichloromethane/petroleum ether, (2-((dimethylamino)methyl)phenyl)(2-((4-methoxyphenyl)azo)-

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5-methoxyphenyl)palladium (**10c**) (0.55 g, 44%): dark yellow crystals (from dichloromethane/petroleum ether); mp 158–160.5 °C dec. Anal. Calcd for $C_{23}H_{25}N_3O_2Pd$: C, 57.3; H, 5.2; N, 8.7. Found: C, 56.95; H, 5.2; N, 8.6. This was followed by bis(2-((4-methoxyphenyl)azo)-5-methoxyphenyl)palladium (**3c**) (0.11 g, 14%): orange-red crystals (from dichloromethane/petroleum ether); mp 195–198 °C dec (lit.[4] mp 204–205 °C). Anal. Calcd for $C_{28}H_{26}N_4O_4Pd$: C, 57.1; H, 4.45; N, 9.5. Found: C, 56.65; H, 4.3; N, 9.35.

From a seond reaction, employing complex **1c** and the lithio compound in a 1:4 molar ratio, further elution with chloroform resulted in the isolation of bis(2-((dimethylamino)methyl)phenyl)palladium (**4**, M = Pd) (18%): colorless needles (from chloroform); mp 188–211 °C [cf. (a) above]; ^1H NMR ($CDCl_3$) δ 7.52 (d, 2 H, H-6), 6.94–7.07 (m, 6 H, H-3–5), 3.84 (s, 4 H, CH_2), 2.60 (s, 12 H, CH_3). Anal. Calcd for $C_{18}H_{24}N_2Pd$: C, 57.5: H, 6.45; N, 7.5. Found: C, 57.4; H, 6.4; N, 7.3.

Insertion Reactions. Azoarene Complexes with Styrene. The following conditions were tried unsuccessfully: Complex **1a** in benzene, 80 °C, 100 h [TLC showed a trace of product, probably 2-(phenylazo)stilbene]; in benzene plus triethylamine, 80 °C, 60 h; in acetic acid, 20 °C, 12 h, then 80 °C, 48 h; (pentane-2,4-dionato)(2-(phenylazo)phenyl)palladium[20] in benzene, 80 °C, 48 h; bis(triphenylphosphine)chloro(2-(phenylazo)phenyl)palladium[21] in benzene, 80 °C, 48 h; complex **10a** in acetic acid, 60–70 °C, 24 h. The last yielded free *N,N*-dimethylbenzylamine and bis[acetoxy(2-(phenylazo)phenyl)palladium] (**1d**) (69%), mp 205–206 °C (lit.[22] mp 208–210 °C); in the other reactions the starting complex was largely recovered.

Bis(2-((dimethylamino)methyl)phenyl)palladium (4, M = Pd) with Styrene. Complex **4** (M = Pd) (0.2 g, 0.53 mmol) and styrene (0.22 g, 2.1 mmol) were stirred in glacial acetic acid (15 mL) at 40 °C for 8 h. After filtration from precipitated palladium, the solution was evaporated and the residue dissolved in chloroform (50 mL), washed with saturated sodium hydrogen carbonate (2 × 20 mL) and water (20 mL), dried, and evaporated. The residue was chromatographed on alumina. Chloroform eluted 2-((dimethylamino)methyl)stilbene[15,23] as a colorless oil (110 mg, 44%): ^1H NMR ($CDCl_3$) δ 7.63 (d, 1 H, J = 16 Hz, =CH—), 7.20–7.72 (m, 9 H, ring H), 6.99 (d, 1 H, —CH=), 3.50 (s, 2 H, CH_2), 2.29 (s, 6 H, CH_3). Anal. Calcd for $C_{17}H_{19}N$: C, 86.0; H, 8.1; N, 5.9. Found: C, 85.5; H, 8.1; N, 6.1.

Bis(2-((dimethylamino)methyl)phenyl)palladium (4, M = Pd) with Carbon Monoxide. Carbon monoxide was passed for 20 h at room temperature through a stirred solution of complex **4** (M = Pd) (0.4 g, 1.06 mmol) in benzene (30 mL). After filtration from precipitated palladium and removal of solvent the residue was shown by ^1H NMR to be a mixture (∼1:2) of the ketone **11** and *N,N*-dimethylbenzylamine. The latter was removed in high vacuum at 50–60 °C. The ketone **11** was purified by chromatography on alumina; chloroform eluted this product (100 mg, 32%) as a colorless hygroscopic oil: ^1H NMR ($CDCl_3$) δ 7.20–7.55 (m, 8 H, ring H), 3.51 (s, 4 H, CH_2), 2.12 ppm (s, 12 H, CH_3); IR (film) 1660 cm^{-1} (CO). Mass spectrum: m/z [relative abundance] 296.1894 [34] (M^+; calcd for $C_{19}H_{24}N_2O$ m/z 296.1889); 251.1284 [63] (M^+ - $HNMe_2$; $C_{17}H_{17}NO$, m/z 251.1310); 250.1217 [62] $C_{17}H_{16}NO$, m/z 250.1232); 208.0906 [58] ($C_{13}H_{12}O$, m/z 208.0888); 207.0804 [56] ($C_{13}H_{11}O$, m/z 207.0810); 206.0721 [42] ($C_{13}H_{10}O$, m/z 206.0732); 180.0896 [63] ($C_{14}H_{12}$, m/z 180.0939); 179.0816 [100] ($C_{14}H_{11}$, m/z 179.0861). This product readily formed a *dimethiodide*. Anal. Calcd for $C_{21}H_{30}I_2N_2O$: C, 43.5; H, 5.2; N, 4.8. Found: C, 42.9; H, 5.3; N, 4.6.

Attempted Reactions of the Benzaldoxime Complex 12.[16] No reaction occurred when this complex was treated at room temperature with styrene [benzene or acetic acid or acetic + trifluoroacetic acids (5:1), 24 h]. Decomposition of the complex only occurred on heating (benzene, 80 °C; acetic acid, 60 °C; 10 h).

Bis[(2-((*N-tert*-butylimino)methyl)phenyl)chloropalladium] (13)[17] **with Methyl Acrylate. (a) In Acetic and Trifluoroacetic Acids.** A mixture of complex **13** (0.5 g, 0.83 mmol) and methyl acrylate (0.285 g, 3.32 mmol) in acetic acid and trifluoroacetic acid (5:1) (20 mL) was stirred for 12 h at 40 °C. After filtration from precipitated palladium the solution was diluted with water (50 mL) and extracted with chloroform (100 mL). The extract was washed with saturated sodium hydrogen carbonate (2 × 30 mL) and water (50 mL), dried ($MgSO_4$), and evaporated. Chromatography on silica gel (60–120 mesh), eluting with chloroform, yielded a colorless oil (160 mg, 51%). Pure methyl 2-formylcinnamate, mp 52–54 °C (lit.[24] m.p. 82 °C), was obtained by crystallization from chloroform/hexane; the observed melting point was unchanged by further crystallization from aqueous methanol: ^1H NMR ($CDCl_3$) δ 10.29 (s, 1 H, CHO), 8.52 (d, 1 H, J = 18 Hz, CH=$CHCO_2Me$), 7.45–8.01 (m, 4 H, ring H), 6.38 (d, 1 H, $CHCO_2Me$), 3.82 (s, 3 H, CH_3). Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.45; H, 5.3. Found: C, 68.9; H, 4.9.

(b) In Toluene and Triethylamine. A mixture of complex **13** (1.0 g, 1.66 mmol), methyl acrylate (1.44 g, 16.6 mmol), triethylamine (3 mL), and toluene (40 mL) was heated under reflux with stirring for 24 h. Evaporation of the filtered solution left product **14** as a faintly yellow oil (0.79 g, ∼100%): ^1H NMR ($CDCl_3$) δ 8.58 (s, 1 H, CH=N), 8.35 (d, 1 H, J = 17 Hz, CH=$CHCO_2Me$), 7.30–7.90 (m, 4 H, ring H), 6.31 (d, 1 H, $CHCO_2Me$), 3.80 (s, 3 H, OCH_3), 1.33 (s, 9 H, C–CH_3); IR (film) 1710 cm^{-1} (CO). Hydrogenation of this product (0.7 g, 2.85 mmol) was performed without purification by using 10% palladium-on-charcoal (50 mg) with methanol (20 mL) as solvent at atmospheric pressure and room temperature. Consumption of the calculated quantity of hydrogen occurred within 1.5 h. Filtration from catalyst and evaporation left an oil and colorless crystals; dissolution in a small volume of ether allowed the former to be separated by filtration from the unidentified solid (∼100 mg). The ether solution was evaporated and the residue chromatographed on silica gel. Chloroform/methanol (9:1) eluted the ester **15** (0.3 g, 42%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.04–7.36 (m, 5 H, ring H), 3.74 (s, 2 H, CH_2N), 3.66 (s, 3 H, OCH_3), 3.03 (br t, 2 H, J = 8 Hz, CH_2CO), 2.69 (br t, 2 H, CH_2), 1.20 (s, 9 H, C–CH_3); IR (film) 1730 cm^{-1} (CO); M^+ m/z 249.1724 (calcd for $C_{15}H_{23}NO_2$ m/z 249.1729).

Complex 13 with But-3-en-2-one. Complex **13** (0.5 g, 0.83 mmol) and methyl vinyl ketone (0.58 g, 8.3 mmol) were stirred in acetic acid (20 mL) at 60 °C for 3 h. The cooled mixture was filtered, diluted with water, and extracted with chloroform [as in (a) above] and the washed and dried extract evaporated. The residue was chromatographed on silica gel (60–120 mesh), eluting with chloroform. A fraction containing 4-acetoxybutan-2-one (90 mg) was followed by 2-acetylindene (**16**) (110 mg, 42%): colorless crystals; mp 61–62 °C (lit.[25] mp 62 °C); ^1H NMR ($CDCl_3$) δ 7.61 (t, 1 H, J = 2 Hz, H-1), 7.24–7.58 (m, 4 H, H-4–7), 3.66 (d, 2 H, H-3), 2.48 (s, 3 H, CH_3).

Crystal Structure Determinations. *cis*-Bis(2-(phenylazo)phenyl)palladium. The compound forms dark red crystals, mp 173–175 °C (Kofler); the crystal selected was bounded by {100}, {010}, and {001}, but another habit seen had {110} and {101} prominent.

Crystal data: $C_{24}H_{18}N_4Pd$, M_r 466.8; triclinic; a = 7.72 (1) Å, b = 9.19 (1) Å, c = 14.96 (1) Å; α = 87.9 (1)°, β = 85.3 (1)°, γ = 70.4 (1)°; V = 996 Å^3; D_{measd} = 1.56 ± 0.02 g/cm^3; Z = 2, D_{calcd} = 1.56 g/cm^3, $F(000)$ = 472; space group $P\bar{1}$; Cu Kα radiation,

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λ = 1.5418 Å; μ(Cu Kα) = 78.65 cm^{-1}; crystal dimensions (perpendiculars from a common center) 0.306 × 0.154 × 0.134 mm. The unit cell chosen is a Niggli-reduced one.

Crystallographic Measurements. The parameters of the unit cell were found from rotation and Weissenberg photographs about *a* with Cu Kα radiation and from precession photographs with Mo Kα (λ = 0.7107 Å) radiation. Data for the layers 0 – 6, *k*, *l* were collected as equi-inclination multiple-film Weissenberg photographs. The intensities for 2083 independent reflections were measured and corrected for absorption at the SERC Microdensitometer Laboratory. Subsequently these were corrected for polarization and Lorentz factors.

Structure Determination. The known molecular weight, the density, and the volume of the unit cell gave $Z = 2$, and the space group was taken as $P\bar{1}$ from the start. A three-dimensional Patterson map gave coordinates for the palladium atom; thereafter, the calculations resembled those described in reference.[32] Refinement was performed by block-diagonal (9 × 9 or 4 × 4) least-squares methods, minimizing $\sum(w\Delta^2)$. With unit weights, isotropic temperature parameters, and omitting hydrogen atoms, refinement converged at $R = 0.0663$; with the weighting scheme $w^{1/2} = 1.0$ if $|F_o| \leqslant 50.0$; otherwise $w^{1/2} = |F_o|/50.0$, and using the imaginary component of anomalous dispersion, $R = 0.0656$; after introduction of H atoms at calculated sites (C–H = 1.08 Å, $U_H = 1.3\ U_C$), $R = 0.0616$. Final interlayer scaling followed (cf. ref 32); parameters for hydrogen atoms were not refined but were included in structure factor calculations, and, after introduction of anisotropic temperature parameters for all non-hydrogen atoms, the final discrepancy ratios were $R = 0.0357$, R' $([\sum(w\Delta^2)/\sum(wF_o)^2]^{1/2}) = 0.0457$, and S $([\sum(w\Delta^2)/(m-n)]^{1/2}) = 1.454$. The most intense reflections may reveal uncorrected extinction. When refinement had converged, a difference Fourier map was computed and searched for peaks of maximum density exceeding ±0.5 e Å^{-3}; within the asymmetric unit seven were found, all negative, with an extreme value of –0.9. None was chemically significant.

The programs used were those of the SCXR series, written by J.A.D.J. and run on a VAX 11/782 computer at the University of Strathclyde.

***cis*-[(2-((Dimethylamino)methyl)phenyl)(2-(phenylazo)phenyl)palladium]. Crystal data**: $C_{21}H_{21}N_3Pd$, M_r 421.8; triclinic, a = 11.154 (4) Å, b = 12.461 (6) Å, c = 14.201 (7) Å; α = 94.64 (4)°, β = 104.13 (4)°, γ = 90.65 (3)°, V = 1906.8 Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centered reflections, λ = 0.71069 Å); space group $P\bar{1}$ (No. 2); $Z = 4$, D_{calcd} = 1.469 g cm^{-3}; μ(Mo Kα) = 9.55 cm^{-1}.

Data Collection. The intensity data were collected on a CAD4 diffractometer in the ω–2θ mode with the ω scan width = (0.85 + 0.35 tan θ)° and the ω scan speed = 1.5–6.7 deg min^{-1} using graphite-monochromated Mo Kα radiation. Over the reciprocal space hemisphere ($1.0 \leqslant \theta \leqslant 25.0°$; $\pm h, \pm k, +l$) 6633 intensities were measured. After data reduction and correction for Lorentz and polarization effects, 4527 reflections had $I > 2\sigma(I)$ and were used in structure solution and refinement. There was little appreciable crystal decay. Since the absorption coefficient μ was comparatively low, no correction was applied for absorption.

Structure Analysis and Refinement. The Pd atoms were readily located by Patterson methods (SHELX84)[33] and the remaining non-hydrogen atoms from subsequent difference Fourier maps phased on the heavy-atom positions. Full-matrix least squares (SHELX76)[34] with all the non-hydrogen atoms anisotropic and the hydrogen atoms in calculated positions gave at convergence R and R_w factors of 0.045 and 0.066, respectively. The weighting scheme with $w = 1/[\sigma^2(F) + 0.0078F_o^2]$ where $\sigma(F)$ is derived from counting statistics gave satisfactory variance analyses. The final difference Fourier map contained two peaks of ca. ±0.6 e Å^{-3} in the vicinity of each of the Pd atoms; otherwise the general noise level of the map was <0.2 e Å^{-3}.

Acknowledgment. We thank Dr. H. M. Elder and his staff at the SERC Laboratory at Daresbury for recording the intensities for **3a** and correcting them for absorption and Dr. A. J. Welch (University of Edinburgh) for access to data collection facilities. The work was made possible by a research grant from the SERC and the participation of T.J. and A.P. by leave of absence from the Politechnika Lodzka and the Politechnika Warszawa, respectively.

Registry No. **1a**, 14873-53-1; **1b**, 20249-93-8; **1c**, 25777-50-8; **1d**, 107079-46-9; **3a**, 108393-18-6; **3b**, 108393-19-7; **3c**, 108393-20-0; *cis*-**4** (M = Pd), 38437-97-7; **9**, 27171-81-9; **10a**, 108346-85-6; **10b**, 108346-86-7; **10c**, 108346-87-8; **11**, 108346-80-1; **11** dimethiodide, 108346-81-2; **12**, 30473-71-3; **13**, 39046-09-8; **14**, 108346-83-4; **15**, 108346-84-5; **16**, 43073-11-6; axobenzene, 103-33-3; palladium chloride, 7647-10-1; 4,4′-dimethylazobenzene, 501-60-0; 4,4′-dimethoxyazobenzene, 501-58-6; *N*,*N*-dimethylbenzylamine, 103-83-3; styrene, 100-42-5; 2-((dimethylamino)methyl)stilbene, 95851-98-2; methyl acrylate, 96-33-3; methyl 2-formylcinnamate, 108346-82-3; but-3-en-2-one, 78-94-4; 4-acetoxybutan-2-one, 10150-87-5.

Supplementary Material Available: Tables of hydrogen atom coordinates for **3a** and **10a**, lists of temperature parameters for their atoms, stereopairs of compounds **3a** and **10a**, in each case seen along the normal to the best plane through Pd and the four atoms to which it is bonded, a stereopair of the contents of the unit cell of **3a** seen down the *a* axis, and an analysis of the conformation of **3a**, comparing derived and experimental values (15 pages); listings of structure factors for **3a** and **10a** (41 pages). Ordering information is given on any current masthead page.

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