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Reactions of cyclopalladated *N*-nitrosoanilines with Sn^{IV} reagents. Crystal structure of the bis cyclopalladated complex *cis*-Pd{ $ONN(CH_3)(C_6H_4)$ }$_2$

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Abstract

A series of cyclopalladated *N*-methyl-*N*-nitrosoanilines, [Pd(μ-X){$ONN(CH_3)$-(C_6H_3Y)}]$_2$, X = OAc, Cl, Y = 4-OCH_3, 4-CH_3, 4-NO_2, 5-CH_3, have been prepared and treated with (i) a variety of reagents to afford mononuclear palladium(II) derivatives, and (ii) $R^1_3SnR^2$ to yield eventually 2-R^2 substituted *N*-methyl-*N*-nitrosoanilines. The tin(IV) reagents, Me_4Sn, $Me_3SnC{\equiv}CPh$, $Bu^n_3SnC{\equiv}C(CH_2)_4$-$CH_3$, $Bu^n_3SnCH{=}CH_2$, and $Bu^n_3SnCH_2CH{=}CH_2$ all effectively transfer the R^2 group to Pd, but, the mechanisms of the transfer reactions are not necessarily all the same. In some cases the presence of additional ligands, such as PPh_3 or $(Ph_2PCH_2)_2$, are required to suppress side reactions, especially the formation of the bis cyclopalladated complex *cis*-Pd{$ONN(CH_3)(C_6H_4)$}$_2$, **5**. The crystal structure of **5** has been determined by X-ray diffraction methods; relevant bond distances (Å) and bond angles (°) are: Pd–N(1) = 2.082(4), Pd–N(3) = 2.078(4); Pd–C(2) = 2.005(4); Pd–C(9) = 1.997(4); N(1)–Pd–N(3) = 99.7(2), N(1)–Pd–C(9) = 168.8(2), N(1)–Pd–C(2) = 79.5(2); C(2)–Pd–C(9) = 102.4(2). It is suggested that the formation of a specific coordination sphere, involving, one cyclometallated ligand, one weakly coordinated ligand, and a monodentate carbon ligand, such as CH_3, leads to production of **5**.

Introduction

The cyclometallation reaction continues to attract interest because it provides a straightforward method of preparing *ortho*-substituted organic aromatic compounds [1]. In recent studies on palladium Schiffs' base, **1**, [2] and palladium and platinum

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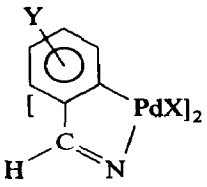
phosphite complexes, **2**, [3] which are potential aldehyde and phenol precursors, we examined structural and synthetic features of cyclometallation chemistry. During these and later studies we have observed the formation of bis cyclometallated com-



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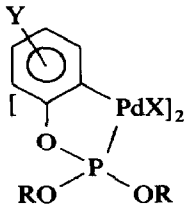

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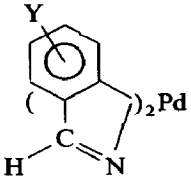

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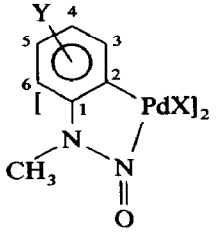
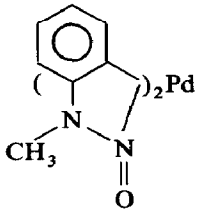


(4)

X = OAc Y **a** = 4-OCH_3
b = 4-CH_3
c = 5-CH_3
d = H
e = 4-NO_2

f X = Cl Y = H
g = I = H

plexes, e.g., **3** and **5**. We comment here on (a) the syntheses of cyclopalladated *N*-nitrosoanilines, **4**, which are potential secondary aniline precursors, (b) the use of organotin compounds as reagents for subsequent transformation of cyclopalladated complexes, and (c) the coordination features necessary for the development of the bis-cyclometallated complexes **5**. The crystal structure of **5**, as determined by an X-ray diffraction study is also reported.



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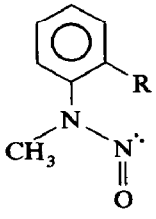

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Results and discussion

Cyclometallation chemistry. The complexes **4** were prepared in 82–98% yield, see Table 1, by treating a nitrosoaniline ligand, e.g. **6**, R = H, with $Pd(OAc)_2$ in

$$Pd(OAc)_2 + \mathbf{6} \xrightarrow[\Delta]{HOAc} \mathbf{4d} + HOAc \qquad (1)$$

Table 1

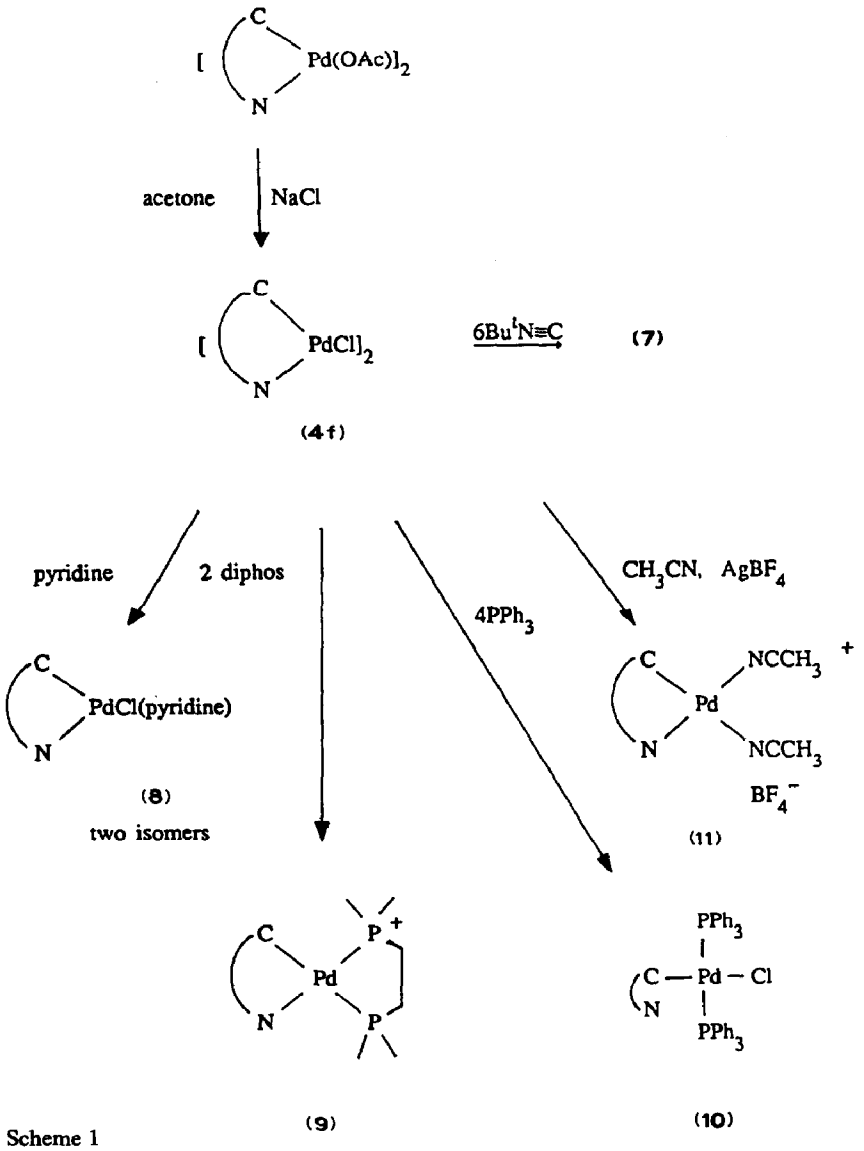
IR [a] and MS [b] data for the *N*-methyl-*N*-nitrosoaniline-derivatives

Compound	Color	MP (°C)	IR	Microanalyses (Found (calcd.) (%))			Yield (%)
				C	H	N	
4a X = ac	red-brown		C=O 1560s				86
4b X = ac	deep-orange		C=O 1563s	38.14 (38.02)	3.84 (3.90)	8.90 (8.86)	96
4c X = ac	deep-orange		C=O 1572s				92
4d X = ac	orange	240 [c]	C=O 1560s	35.96 (36.09)	3.35 (3.13)	9.32 (9.44)	91
4f X = Cl	yellow	245 [c]	Pd–Cl 344m 314m				92
4g X = I [g]	light-yellow			22.82 (22.69)	1.91 (1.85)	7.60 (7.27)	98
4e X = ac	brown-black		C=O 1553s NO_2 1519s 1340s				82
7 [h]	yellow		Pd–Cl 253m [e] C≡N 2333s 2204s [f] C≡N 1636s 1612s [f]	50.20 (50.62)	6.51 (6.69)	13.30 (13.31)	
8	yellow	159–160 [c]	Pd–Cl 349m 315m [d]				94
9 [i]	yellow	165 [c]					78
10	yellow		Pd–Cl 285m				91
11	yellow	220 [c]	C≡N 2323s 2291s				95

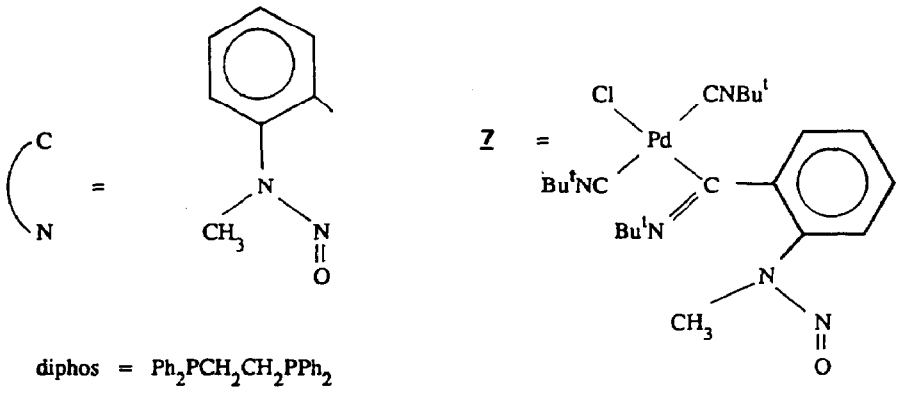
[a] ν in cm^{-1}, s = strong, m = medium, w = weak. [b] C=O indicates bridging acetate carbonyl. [c] With decomposition. [d] Two isomers exist in the solid. [e] CsI. [f] Solution in $CHCl_3$; as CsI pellet: C≡C, 2200s, 2220w; C=N, 1637s, 1620s, 1610s. [g] I analysis, 34.44 (34.70). [h] Cl analysis, 6.73 (6.63), mol. wt in CH_2Cl_2 526.4 (506.8). [i] δ ^{31}P ($CHCl_3$): 42.2, 59.0, $^2J(P,P) = 30.5$, δ ^1H, 3.35, N–CH_3; 1.8–2.4, PCH_2CH_2P.

refluxing acetic acid. Although we routinely allowed the reaction to proceed for 30 min, ^{1}H NMR studies in CD_3CO_2D showed the reaction to be complete within 10 min for **6**, R = H. The cyclometallation also proceeds smoothly at 60 °C in the presence of NaOAc. Previous synthetic studies [4] involving *N*-methyl-*N*-nitrosoaniline and Na_2PdCl_4 in methanol afforded **4**, Y = H, X = Cl, in only 46% yield, suggesting that $Pd(OAc)_2$ may be generally more suitable as a starting material. The cyclometallation to give **4** is not markedly dependent on the nature of the aryl substituent, Y, and proceeds in high yield with either electron-releasing and electron-withdrawing groups *para* to the nitrogen.

The parent complex, Y = H, X = OAc, can be converted into a series of mononuclear derivatives, as shown in Scheme 1. Complex **7** is of interest in that it



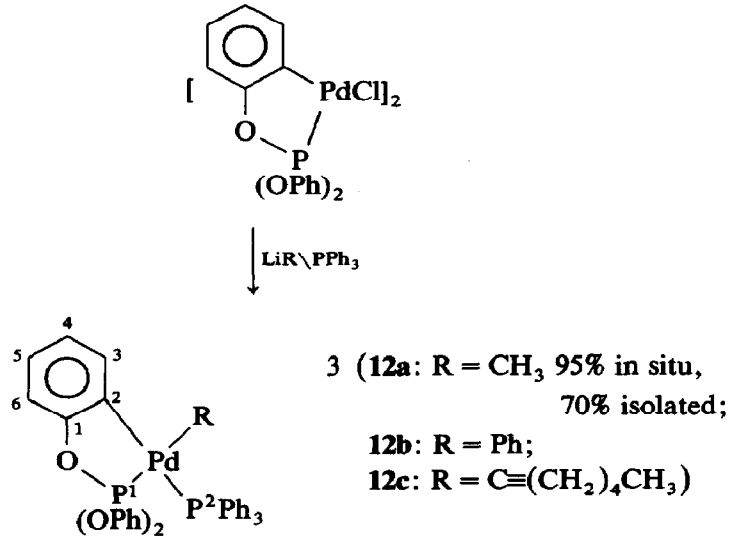
Scheme 1



Scheme 1 (continued)

contains two *trans* Bu^{t}NC ligands and one Bu^{t}NC which has undergone insertion into the Pd–C carbon of **4f**. The identity of **7** is based on its elemental analysis, and molecular weight, IR, and NMR spectroscopic studies. Insertions of isonitriles have been reported with cyclopalladated Schiffs' base as starting material [6]. Tables 1 and 2 list selected ^{1}H NMR, IR, and microanalytical data for the cyclometallated nitrosoamine complexes.

The reaction of **4f** with Grignard and lithium reagents would be expected to lead to 2-substituted organic compounds [7]; however, in our hands, with PPh_3 present to stabilize the formed Pd^0, yields were poor; e.g., **4f** reacted with CH_3Li to afford **6**, Y = H, R = CH_3, in 14% yield. Attempts to prepare the phenyl or butyl analogs were also unsuccessful. A similar procedure with the cyclopalladated phosphite **2**, X = Cl, R = Ph, was somewhat more successful, as shown in Scheme 2, but did not yield 2-substituted phosphite derivatives.



Scheme 2

Table 2

^{1}H NMR [a] data for selected cyclometallated nitrosoamine complexes [b]

Complex	H(3)	H(4)	H(5)	H(6)	CH_3–N	CH_3–COO	other
4a X = ac	6.70(2.3)		6.57(8.5, 2.3)	6.40(8.5)	2.85	2.22	3.83 (CH_3O–)
4b X = ac	7.00(~1 [c])		6.85(7.9, ~1 [c])	6.40(7.9)	2.78	2.26	2.32 (CH_3–Ac)
4c X = ac	7.08(7.89	6.67(7.8, ~1 [c])		6.36(~1 [c])	2.76	2.22	2.31 (CH_3–Ac)
4d X = ac	7.24(7.6, 1.2)	6.97(7.6, 7.6, 1.2)	7.09(7.6, 7.6, 1.2)	6.53(7.6, 1.2)	2.79	2.25	
4e X = ac	8.00(1.6)		8.02(8.3, 1.6)	6.7(8.3)	2.95	2.30	
8 [d]	8.15 [e](7.5)	7.11 [e](7.5, 7.5)	7.23(7.5, 7.5, 1.2)	6.93(7.5, 1.2)	3.55		8.79 [e](5) 2H; 7.45 [e](5, 7.5), 2H; 7.85 [e](7.5), 1H (PY)
10 [h]	7.16(7.5, 1.0)	6.50(7.5, 7.5, 1.4)	6.68(7.5, 7.8, 1.0)	6.25(7.8, 1.4)	2.60		7.20–7.45, m, 30H (PPh_3)
7	7.85(7.6, 1.3) [f]	7.38(7.6, 7.6, 1.3) [f]	7.48(7.6, 7.6, 1.3) [f]	7.18(7.6, 1.3) [f]	3.37		1.47, s, 27H (^{t}Bu) [g]

[a] $CDCl_3$, RT. [b] Numbering scheme as shown in **4**, [c] Resonance is broad. [d] Pyridine assumed *trans* to C(2). [e] Broad (LB ~ 3–4 Hz). [f] Assignment tentative. [g] At 233 K: 1.42s, 18H, 1.40s, 9H. [h] δ ^{31}P = 21.1.

Table 3

NMR spectroscopic data [a] for **12a–12c**

		12a		**12c** [b,c]	**12b**
^{31}P	P^1	148.8		144.8	146.2
	P^2	28.3		20.5	20.2
	^2J(P,P)	32.0		34.9	34.5
^1H	H(3)	7.74		8.60	
		(0.5)[6.0]		(0.8)[7.0]	
	Pd–CH_3	0.53		2.00 α-CH_2	
		(9.8)[7.3]		0.69 CH_3	
^{13}C	CH_3	11.5	Pd–*C*≡C	103.4	
		(141.0)[11.0]		(188)[29.3]	
			Pd–C≡*C*	113.3	
				(46.4)	
	C(1)	160.2		158.0	
		(25.5)[5.5]		(28)	
	C(2)	144.7		142.2	
		(15.5)[114.5]		(9.8)[116]	
	C(6)	112.3		111.9	
		(14.0)[3.6]		(18.3)[4.9]	
^{13}C PPh_3 [d]	C(1′)			133.0	
				[42.0]	
	C(2′)	134.6		134.9	
		[13.0]		[12.1]	
	C(3′)	128.7		128.6	
		[10.0]		[9.9]	
	C(4′)	129.8		130.0	

[a] Chemical shifts in ppm, coupling constants in Hz, values in parenthesis are J values to P^1, in square brackets J values to P^2. [b] 243 K. [c] δ ^{13}C for n-pentyl chain, starting from α-CH_2 through to CH_3: 21.5, 29.6, 31.3, 22.8, 14.5, respectively. [d] For PPh_3.

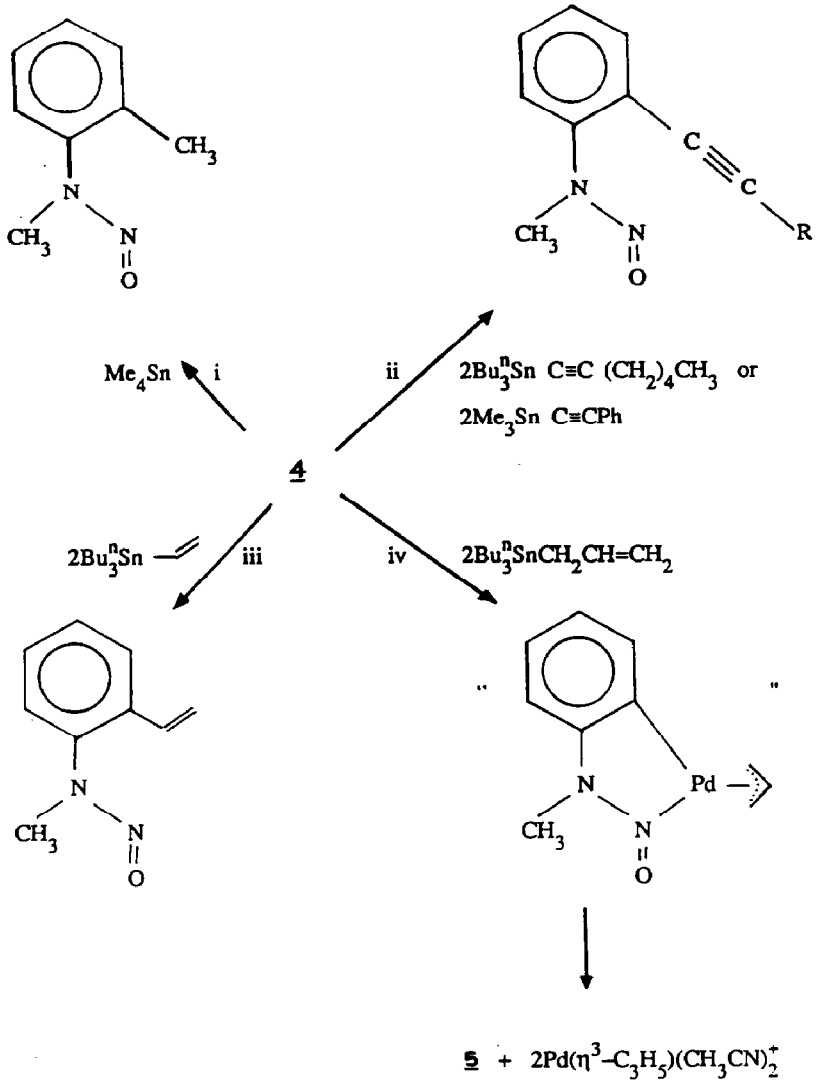
Complexes **12** are only moderately stable in solution over longer periods, but can be readily characterized by NMR spectroscopy (Table 3). Specifically, the complex geometry is readily determined from the ^2J(P,P) values derived from the $^{31}P\{^1H\}$ NMR spectra [8]. The main point in connection with this Grignard-type chemistry is that for neither the nitroso nor the phosphite cyclometallated complexes were we able to obtain the desired organic product cleanly, and this prompted us to consider the use of alkyltin reagents, for which there is precedent in palladium chemistry [9–12].

Reactions of tin compounds. In Scheme 3 we show some reactions of Me_3SnR and Bu^n_3SnR reagents.

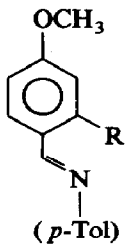
In general the alkyl tin reagents are easily handled, since they are not especially hygroscopic or oxygen-sensitive and are commercially available or easy to make.

The methylation reaction was investigated in some detail and the following observations are relevant:

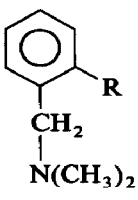
(i) This type of methylation has some generality, and was successfully used to prepare the imine and amine compounds **13a** and **14a**, respectively, from acetate-bridged complexes.



Scheme 3. Reactions of **4**. X = OAc, with alkyl tin reagents. i. Acetone solution, 10 equivalents of Me_4Sn, faster with MeI present, with X = OAc a good yield was obtained for the analogous reaction with an OCH_3 group *para* to the nitrosoamine. ii. 4 equivalents of $(Ph_2PCH_2-)_2$, X = OAc, RT, 18 h. iii. Acetone solution, 4 equivalents of PPh_3, X = OAc, RT, 18 h. iv. CH_3CN solution, X = Cl, $AgBF_4$ added.



(**13a**: R = CH_3 (100% in situ);
13b: R = C≡CPh (100% in situ))



(**14a**: R = CH_3 (79%, isolated);
14b: R = C≡CPh (65% in situ))

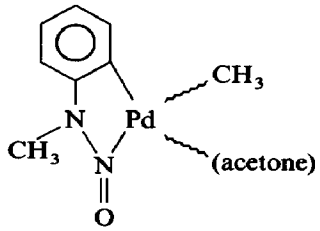
(ii) At least 5 equivalents of Me_4Sn are required for essentially quantitative conversion.

(iii) The Cl-bridged complexes react much more slowly.

(iv) Addition of PPh_3 suppresses the methylation.

(v) The kinetics are qualitatively similar in acetone, chloroform, and benzene.

(vi) Monitoring the progress of the reaction by ^1H NMR spectroscopy reveals the presence of an intermediate Pd–CH_3 complex (δ CH_3, 0.31), to which we assign the structure **15** *. Pd–CH_3 complexes are not very stable, but a number are known [13,14].



(15)

Complex **15** reverts to starting material when the reaction solution is concentrated and the Me_4Sn removed. This suggests that there is an equilibrium, as shown in equation 2, and that the presence of an excess of the tin reagent assists the

$$\mathbf{4d} + Me_4Sn \rightleftharpoons \mathbf{15} + Me_3SnOAc \quad (2)$$

(X = OAc)

formation of **15**. In a typical reaction mixture (initially 0.05 mmole **4d**, 0.5 mmole Me_4Sn, 2.5 ml acetone-d_6), after 24 h at room temperature, ^1H NMR spectroscopy revealed the presence of 10% of unchanged **4d**, 45% of **15**, 45% of *N*-(2-methylphenyl)-*N*-methylnitrosoamine, **16**, and 90% of Me_3SnOAc. At the end of the reaction, which we depict in Scheme 4, there was a small amount of the bis cyclometallated complex **5**. The development of products and disappearance of **4a**, as monitored by ^1H NMR spectroscopy are shown in Fig. 1.

(vii) Since a color change occurs during the reaction, the development of **15** (λ_{max} 385 nm, $\epsilon = 1375\ M^{-1}\ cm^{-1}$) from **4d** ($\lambda_{max}$ 445 nm, $\epsilon = 2450\ M^{-1}\ cm^{-1}$) can be monitored by UV-VIS spectroscopy (see Fig. 2), and an isosbestic point at 413 nm observed.

(viii) Immediate mixing of Me_4Sn and **4d**, X = OAc in acetone gives **15** more slowly than first stirring a solution of Me_4Sn in acetone at 35 °C for 2 h and then adding **4d**. When the second method is used, variation of the Me_4Sn concentration by a factor of 4 reveals a roughly linear dependence of the rate of appearance of **15** on the concentration of Me_4Sn.

(ix) Addition of styrene, a radical trap, suppresses the reaction. A reaction at room temperature in the presence of azoisobutyronitrile (which generates free radical when warmed [15]) had no effect. Addition of CCl_4 accelerates the reaction, although the chemistry is complicated by the formation of additional products. Irradiation with UV light ($\lambda = 256$ nm) accelerates the reaction by 20–50%.

* A dimer involving nitroso oxygen bridging cannot be excluded. The curly line indicates uncertain geometry. An analogous complex, **15a**, was formed from the 4-OCH_3 complex **4a**.

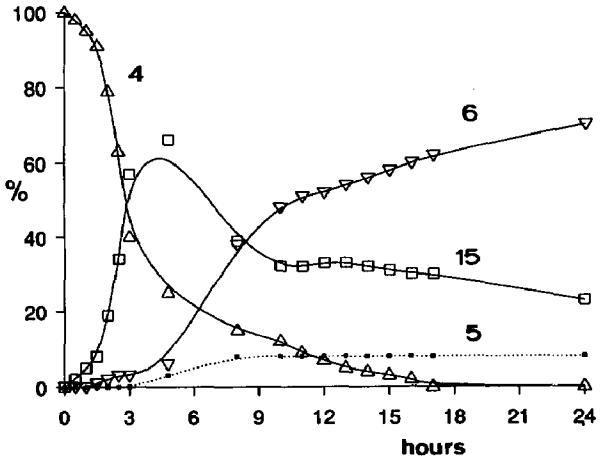
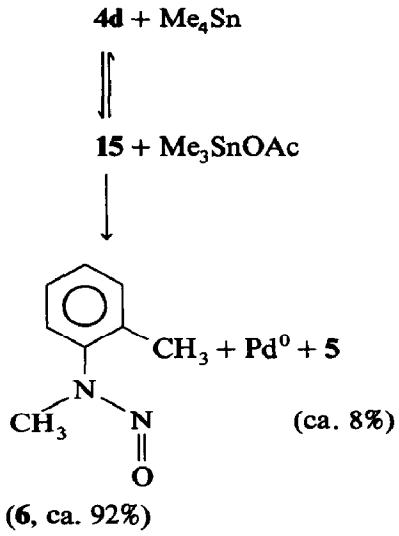


Fig. 1. Percentages of species present at various times, as indicated by ^{1}H NMR spectroscopy, in the reaction of **4d**, with an excess of Me_4Sn to give **15** and Me_3SnOAc (ca. 3 h) and then eventually 92% **6**, R = CH_3 and 8% **5** (48 h); acetone-d_6, 295 K, $[Pd]_{total}$ 0 0.0186 *M*; plot of mole per cent against time.

(x) Use of an excess of CH_3I in acetone leads to clean formation of **15** within minutes, and product **16** is formed, within a few hours. The presence of **4g**, X = I, is detected. When an excess of $^{13}CH_3I$ or CD_3I is employed, ^{13}C or ^{1}H NMR analysis reveals that product **16** contains ca. 55% of H and 45% of ^{13}C (or D) in the 2-CH_3 group (based on relative integrals of signals from aromatic and CH_3 protons). Use of an excess of CH_3I with **4d**, X = Cl, gives only **4g**, X = I, in quantitative yield. The ^{1}H spectrum contains a singlet at $\delta = 0.87$, consistent with the presence of ethane.

Observations vii–x suggest free radical routes for the formation of intermediate **15**. The reactions with CH_3I, involving its relatively rapid production of product **16**



Scheme 4

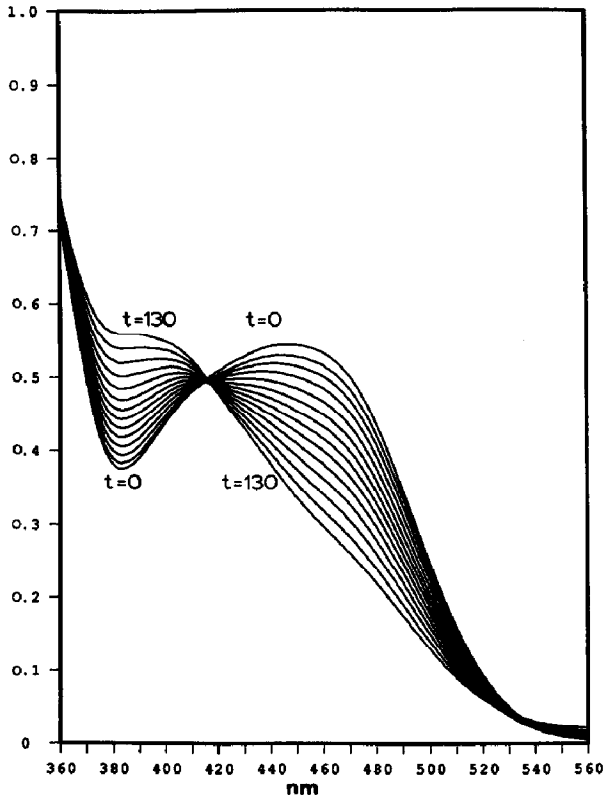
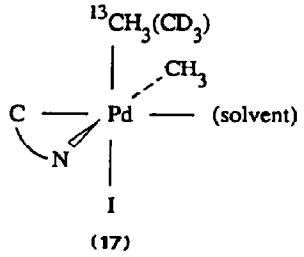


Fig. 2. Formation of **15** as a function of time. A solution of Me_4Sn in acetone was stirred for 2 h at 35 °C, complex **4** then added, and the reaction monitored for 130 min by recording the UV/VIS spectra at 10 min intervals. $[Pd]_{total} = 0.0048$ *M*, $[Me_4Sn] = 0.195$ *M*.

are interesting. From various spectroscopic observations we assume that the reductive elimination **15** → **16** is the slow step *. Thus, it is conceivable that the acceleration of the formation of the final product, **16**, arises from oxidative addition of methyl iodide to a cyclometallated methyl Pd^{II} complex to give the transient species **17**, a process for which there is reasonable precedent [14], followed by reductive elimination to give the product **16**.



(17)

* Complex **15** may not be directly involved, i.e., it may be transformed into another species before **16** appears. We suggest only that the appearance of **15** is not rate determining.

It should be noted that the intermediacy of **17** would account for the presence of a ca. 1 : 1 ratio of CH_3 and $^{13}CH_3$ (or CD_3) in the product formed from $^{13}CH_3I$ (or CD_3I).

The essence of these methylation reactions is that the cyclometallated complex **4d**, containing a good leaving group such as acetate, is methylated by Me_4Sn to give **16**, in a reaction that is accelerated by addition of methyl iodide.

Reaction ii of Scheme 3 depicts two separate processes: a) reaction of complex **4d**, X = OAc, with $Me_3Sn{\equiv}CPh$ and two equivalents of diphos, $(Ph_2PCH_2)_2$, per Pd, and b) reaction of complex **4d**, X = OAc, with $Bu^n_3SnC{\equiv}C(CH_2)_4CH_3$ and again two equivalents of diphos per Pd, Both reactions proceed quantitatively during ca. 5 h to give the 2-substituted organic compounds and R_3SnOAc, R = Me or Bu^n. Work-up in the former case gave a 51% isolated yield.

The generality of this type of reaction is supported by the observation of analogous reactions of cyclopalladated imines and benzylamines with $Me_3SnC{\equiv}CPh$ to give compounds **13b** and **14b**, identified in situ by ^1H NMR. We note that Stader and Wrackmeyer [16] isolated $Pd(C{\equiv}CR)(SnClMe_2)(dppe)$ from the reaction of $PdCl_2(dppe)$ with $SnMe_2(C{\equiv}CR)_2$.

The vinylation reaction, iii, was monitored by ^1H NMR spectroscopy, which revealed ca. 70% conversion into the 2-vinyl nitrosoamine after ca. 18 h at room temperature. Approximately 60% conversion was achieved by using diphos instead of PPh_3; interestingly, in the absence of phosphine additives, there is essentially quantitative conversion into the bis cyclometallated complex **5** (50% based on Pd).

For reaction iv, allylation with $Bu^n_3SnCH_2CH{=}CH_2$, we find rapid formation of **5** involving transfer of allyl to Pd. However, when the allylation was carried out in CD_2Cl_2 at ca. −78° C there was slow but quantitative formation of **18** (within 14 days), characterization of which was straightforward at −50° C (see Fig. 3).

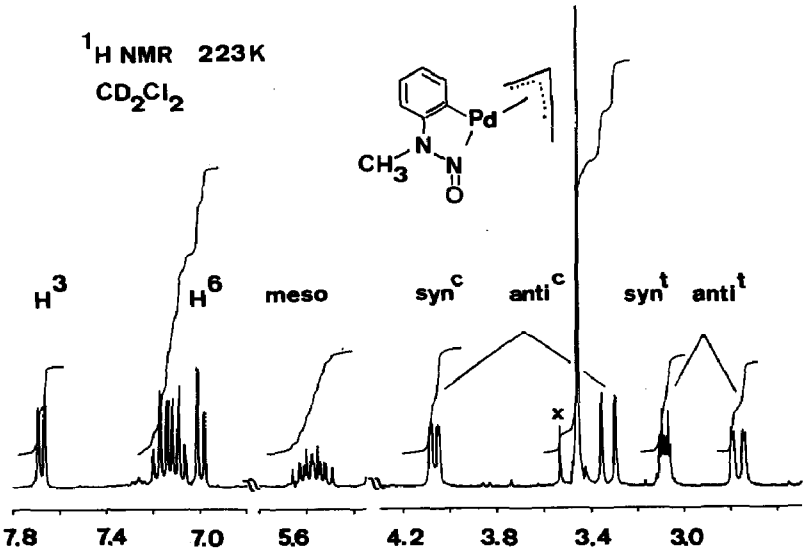
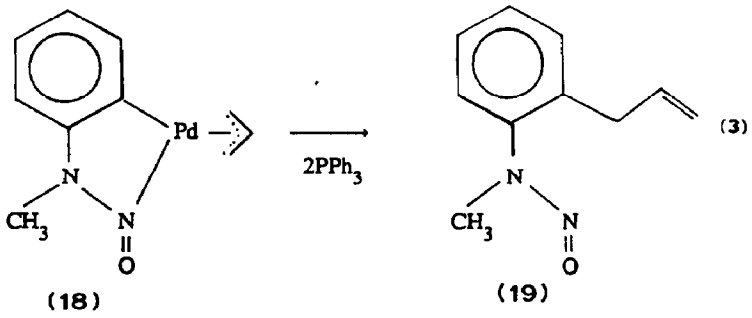


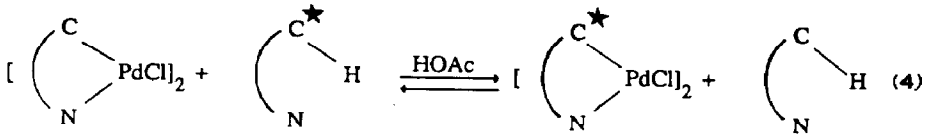
Fig. 3. The ^1H NMR spectrum of the intermediate **18** at 223 K (WM-250, CD_2Cl_2). *syn*^{c}, *anti*^{c}, *syn*^{t}, *anti*^{t} refer to *syn* and *anti* protons *cis* or *trans* to N=O. X = impurity.



The ^1H and ^{13}C NMR data for this and other cyclometallated complexes are given in Table 4. Addition of 2 equivalents of PPh_3 per Pd and setting the solution aside at room temperature for 1 day gave a solution which contained ca. 65% of the 2-allyl nitrosoamine, **19**. A similar result was obtained starting from **4d**, X = OAc, PPh_3, and $Bu^n_3SnCH_2CH{=}CH_2$ in CD_2Cl_2 at room temperature. Obviously, it is possible to transfer the allyl to palladium, but, the reductive elimination to afford **19** is slower than the reaction to give **5**, unless PPh_3 (or another suitable ligand) prevents formation of **5**. Before leaving this account of the allylation we note that, in our hands, $Bu^n_3SnCH_2CH{=}CH_2$ was found to react with Na_2PdCl_4 in methanol to give $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ in high yield; the value of this approach was recognized previously [17]. It is evident that the $R^1_3SnR^2$ reagents examined can be used effectively for the transformation of cyclopalladated *N*-nitrosoaniline, Schiffs' bases, and *N*,*N*-dimethylbenzylamines to 2-substituted organic derivatives. However, the mechanism is not simple, and not every reagent is effective. In particular, we note that **4d**, X = OAc, does not react with Et_4Sn, Bu^n_4Sn or Ph_4Sn.

Conditions for the development of 5. Before speculating on the way in which **5** is formed we first consider some background information. Complex **5** and related bis cyclometallated compounds, e.g., **20**–**24** can be made by use of Grignard or lithium reagents in a conventional manner [18–22]. These complexes all possess a *cis*-MC_2L_2 coordination sphere in the solid state (C = aryl carbon, L = N or O ligand).

Our complex **5** is formed in several reactions as the main product (in allylation) or a side product (in methylation), presumably through some disproportionation process. Related reactions involving transfer of a cyclometallated ligand, depicted generally in equation 4, have been observed by Ryabov and co-workers [22]. This



exchange reaction appears to operate with benzylidine anilines, *N*,*N*-dialkylbenzylamines, and 8-methylquinoline, among others [22], with cyclometallated *N*,*N*-dialkylbenzylamines. A mechanism involving "cleavage of the Pd–N bond ... followed by acidolysis of the Pd–C bond" has been suggested [22a]. Granell et al. [23] made similar observations in the Schiff's base cyclometallation of palladium, again in HOAc as solvent. Van der Ploeg et al. [24] reported disproportionation of *cis*-

Table 4

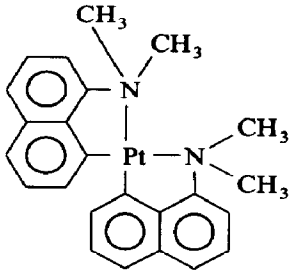
NMR data [a] for the products formed in reaction with the tin(IV) compounds.

		CH_3 groups		Others/comment
(i) From Me_4Sn				
$ONN(CH_3)(2\text{-}CH_3C_6H_4)$				
	^1H	N–CH_3	3.40	two isomers [b]
				major/minor = 88/12,
		2-CH_3	2.26	minor isomer, N–CH_3, 4.05
				2-CH_3, 2.00
	^{13}C	N–CH_3	35.3	minor isomer, N–CH_3, 40.0
		2-CH_3	18.3	2-CH_3, 17.9
$ONN(CH_3)(2\text{-}CH_3,4\text{-}OCH_3C_6H_3)$				
	^1H	N–CH_3	3.36	minor isomer, N–CH_3, 4.04,
		2-CH_3	2.22	2-CH_3, 2.06, O–CH_3, 3.80
		O–CH_3	3.84	
	^{13}C	N–CH_3	35.6	minor isomer, N–CH_3, 41.0,
		2-CH_3	18.3	2-CH_3, 18.0, O–CH_3, 55.5
		O–CH_3	55.6	
13a	^1H	2-CH_3	2.55	N–Aryl CH_3, 2.37
		O–CH_3	3.84	C*H*=N, 8.66
	^{13}C	2-CH_3	21.0	CH_3(tolyl) = 19.7
		O–CH_3	55.3	*C*H=N, 157.8
14a	^1H	N–CH_3	2.23	CH_2, 3.36
		2-CH_3	2.36	
	^{13}C	N–CH_3	45.5	CH_2, 62.0
		2-CH_3	19.1	
15 (15a) [c]	^1H	Pd–CH_3	0.31 (0.30)	
		N–CH_3	3.52 (3.50)	
		H(3)	7.43 (7.04)	
(ii) From $R^1_3Sn\text{-}C{\equiv}CR^2$ [d]				
$ONN(CH_3(2\{C{\equiv}CPh\}C_6H_4)$				
	^1H	N–CH_3	3.57	
	^{13}C	N–CH_3	35.4	*C*≡C, 85.2, C≡*C*, 95.5
				C(1), 143.7, C(2), 119.1
				major isomer (ca. 94%)
$ONN(CH_3)(2\{C{\equiv}C(CH_2)_4CH_3\}C_6H_4)$				
	^1H	N–CH_3	3.48	major isomer (ca. 95%)
13b [e]	^1H	O–CH_3	3.89	C*H*=N, 9.03
		C–CH_3	2.37	
	^{13}C	O–CH_3	55.8	*C*H=N, 157.8,
		C–CH_3	21.3	*C*≡C, 86.4, C≡*C*, 95.3
14b [f]	^1H	N–CH_3	2.33	CH_3, 3.69
	^{13}C	N–CH_3	45.7	CH_2, 61.9,
				C≡C, 88.0, C≡*C*, 93.5
				C(1), 140.7
(iii) From Bu^n_3SnR (R = vinyl, allyl)				
$ONN(CH_3)(2\{C_2H_3\}C_6H_4)$ [g]				
	^1H	N–CH_3	3.36	two isomers
		$CH^A = CH^cH^t$		major/isomer ca. 90/10
		H^A	6.57	minor isomer N–CH_3, 4.06
		H^c	5.36	
		H^t	5.75	
18 [h]	^1H	N–CH_3	3.46	H(3), 7.68, H(4), 7.09.
	^{13}C	N–CH_3	30.5	H(5), 7.17, H(6), 7.00
		C^c	73.5	allyl protons 5.57 (*meso*)
		C^t	43.5	4.06, 3.33, 3.08, 2.77
		C^{meso}	121.4	

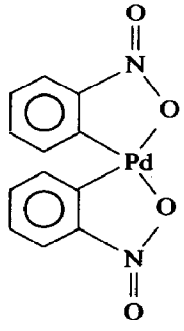
Table 4 (continued)

		CH_3 groups		Others/comment
(iii) From Bu^n_3SnR (R = vinyl, allyl)				
$ONN(CH_3)(2\{CH_2CH{=}CH_2\}C_6H_4)$				
	^1H	N–CH_3	3.35	CH_2, 3.31
		$CH^ACH^cCH^t$		$^3J(H^A, H^t) = 17$
		H^A	4.96	$^3J(H^A, H^c) = 10$
		H^c	5.04	
		H^t	5.85	
$Pd(\eta^3\text{-}C_3H_5)_2$ [i]	^1H	H^{meso}	5.06	exists as two isomers; major/
		H^{syn}	4.08	minor ca. 3/1, minor isomer:
		H^{anti}	2.36	H^{meso}, 4.93, H^{syn}, 3.85, H^{anti},
	^{13}C	C^{meso}	115.1	2.52, C^{meso}, 115.6
		CH_2	54.8	CH_2, 54.0

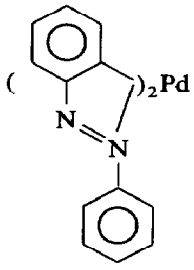
[a] Chemical shifts in ppm, $CDCl_3$ unless otherwise stated. [b] Isomers arise from two possible orientations of –N=O relative to either the CH_3 or phenyl moiety. Major isomer has N=O facing CH_3 group. [c] **15a** is the 4-OCH_3 analog. Me_3SnOAc; ^1H (acetone-d_6) $Me_3SnOCOCH_3$, 1.87, 3H, Me_3SnOAc, 0.47, 9H, $^2J(Sn, H) = 58.0$. in ($CDCl_3$) 2.03, 3H, 0.53, 9H, $^2J(Sn, H) = 58.4$ Hz. [d] $\nu(C{\equiv}C) = 2227\ cm^{-1}$. [e] $\nu(C{\equiv}C) = 2210\ cm^{-1}$, MS: $m/e = 325$ (molecular ion). [f] $\nu(C{\equiv}C) = 2214\ cm^{-1}$, MS: $m/e = 235$ (molecular ion). [g] H^c = *cis* to H^A, H^t = *trans* to H^A. [h] Allyl protons assigned as shown in figure. C^c = allyl *cis* to NO, C^t = allyl *trans* to NO. [i] CD_2Cl_2, 208 K.



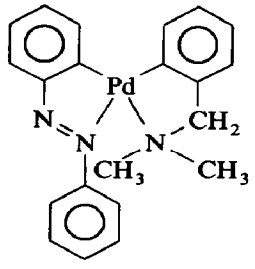
(**20** [18])



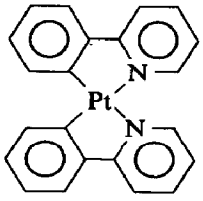
(**21** [19])



(**22** [20])



(**23** [20])

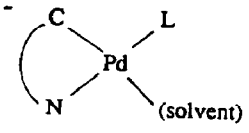


(**24** [21])

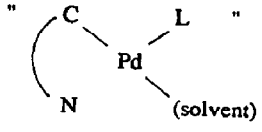
$(2Me_2NCH_2C_6H_4)_2Pd$ in the presence of $Hg(OAc)_2$, TlOAc, or $Pd(OAc)_2$ (eq. 5), thus demonstrating that the presence of an obvious proton source is not necessary

$$Pd(OAc)_2 + cis\text{-}(2Me_2NCH_2C_6H_4)_2Pd \xrightarrow{CHCl_3} [Pd(\mu\text{-}OAc)(2\text{-}Me_2NCH_2C_6H_4)]_2 \quad (5)$$

for this type of exchange. In an earlier study on the carbonylation of cyclopalladated benzylidene anilines [2a], starting from $[Pd(\mu\text{-}OAc)(m\text{-}NO_2C_6H_3CH{=}N(p\text{-}Tol)]_2$, we noted the appearance of $Pd\{m\text{-}NO_2C_6H_3CH{=}N(p\text{-}Tol)\}_2$, under conditions in which formation of the organic product was slow. We have made similar observations in the carbonylation of complex **4** [25]. It is relevant to note the cases in which such bis complexes are not formed, e.g., the reactions with nitrogen, phosphorus and isonitrile ligands shown in Scheme 1 and the related reactions with CN^- [25]. In vinylation and acetylide-formation, the presence of phosphine ligands suppresses the formation of **5**. Furthermore, cyclometallated complexes such as the bis acetonitrile, **11**, or bis solvent complexes with acetone, also give no **5**. These observations taken together suggest that **5** is produced only when one coordination site becomes available and the second is occupied by a carbon ligand arising from either methylation, allylation, or carbonylation. This intermediate, of type **25**, might then give **26**. Reaction of **25** with **26**, in a bimolecular transition state related to



(25)



(26)

L = CH_3, η^1-$CH_2CH{=}CH_2$, CO *

that postulated by Eaborn and co-workers [26], would afford **5** and a PdL_2 species, e.g., $Pd(\eta^3\text{-}C_3H_5)_2$ or $Pd(CO)_2$, which might or might not be stable. There is ample precedent for cleavage of the Pd–N bond [4,6,27]. Clearly, the presence of strong donor ligands prevent formation of significant quantities of **25** and **26**, and since the Pd–N bond must be broken before transfer, it is likely that the formation of

* **4g**, THF, $AgBF_4$, (–AgCl) followed by $NaOCH_3$ and then CO (1 atm) gives 100% (50% based on Pd) **5**. L is possibly methoxide.

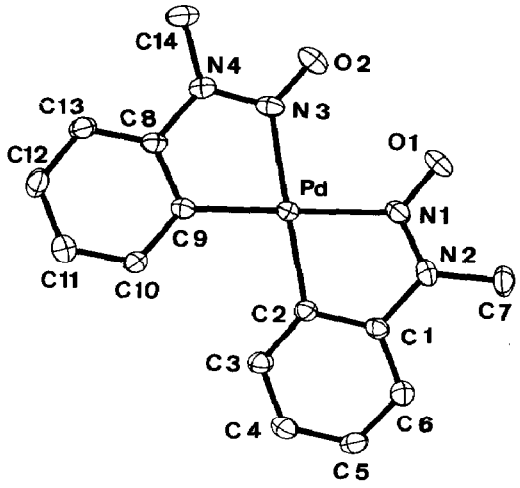


Fig. 4. ORTEP view of complex **5**.

$Pd(\widehat{CN})_2$ is not always fast, so that reaction conditions can be chosen to avoid its formation. Although **5** may prove to be synthetically useful, it appears at present, that it is formed only under rather special conditions.

Molecular structure of 5. In view of our interest in the bis cyclometallated nitrosoamine complex, **5**, we have determined its crystal structure by an X-ray diffraction study. A view of the structure is presented in Fig. 4.

The coordination around the metal is distorted square planar, with Pd–C(2) and Pd–C(9), 2.005(4) and 1.997(4) Å, respectively, and Pd–N(1) and Pd–N(3) are 2.082(4) and 2.078(4) Å, respectively. These distances can be compared with those given for the model complexes **21–24** in Table 5. The coordination angles N(1)–Pd–N(3), 99.7(2)°, C(2)–Pd–C(9), 102.4(2)°, N(1)–Pd–C(2), 79.5(2)° and N(3)–Pd–C(9), 79.8(2)° are as expected. Table 6 gives a selected list of bond lengths and bond angles, and Tables 7 and 8 list atomic coordinates and crystallographic details, respectively.

In addition to the structural features cited above, several aspects are noteworthy:

(i) The molecule is not planar, the two nitroso-oxygens being +0.16, O(1) and −0.20, O(2) Å, above and below the Pd, N(1), N(3) plane, respectively. The angle O(1)–N(1)–N(3)–O(2) is 17°. There may be electronic reasons for this distortion, involving electron–electron repulsion due to some $^{+}N{=}N{-}O^{-}$ delocalization, but we note that the O(1)–O(2) separation, 3.116(7) Å, is not especially short. It is of interest that the angle between the planes defined by the two individual cyclometallated ligands, e.g., between the two phenyl rings, is 152°. The origin of the ca. 17° angle mentioned may be steric in nature, and is perhaps found in the rather short separation of ca. 1.9 Å between the inner protons on C(3) and C(10) (assuming C–H = 1.08 Å). Since planarity of the phenyl rings would result in compression of the C(3)–H(3) and/or C(10)–H(10) bonds, the molecule is distorted.

(ii) The values of the C(8)–N(4), 1.435(6) and C(1)–N(2), 1.440(6) Å distances suggest that these bonds are single, whereas the distances N(1)–N(2), 1.301(7), and

Table 5

Selected bond lengths for **5** and **21–24**

Complex	M–C, Å		M–N, Å		Ref.
5	1.997(4)	2.005(4)	2.078(4)	2.082(4)	this work
21, M = Pd	2.028(3)	2.039(4)	[a]		[19]
22, M = Pd	2.000(7)	1.998(7)	2.131(6)	2.133(6)	[20]
23 [b], M = Pd	1.992(6)	1.997(7)	2.116(5)	2.193(5)	[20]
	azo	amine	azo	amine	
	1.985(6)	1.990(6)	2.104(5)	2.198(5)	
	azo	amine	azo	amine	
24, M = Pt	1.984(4)	2.002(3)	2.125(3)	2.128(3)	[21]

[a] Pd–O, 2.130(5) Å, 2.158(5) Å. [b] Two molecules.

N(3)–N(4), 1.331(6) Å, respectively, are intermediate between N–N single (1.45 Å [28]) and N=N double (1.25 Å [28]) bonds, and suggest some multiple bond character. The N–O bond lengths, N(3)–O(2), 1.226(5) and N(1)–O(1), 1.246(6) are consistent with a rather long –N=O, double bond (ca. 1.20 Å [28]). Shaw and coworkers have presented [4] details of the molecular structure of the cyclometal-

Table 6

Bond lengths (Å) and angles (°) for **5**

Pd–N(1)	2.082(4)	N(1)–Pd–N(3)	99.7(2)
Pd–N(3)	2.078(4)	C(2)–Pd–C(9)	102.4(2)
Pd–C(2)	2.005(4)	N(1)–Pd–C(2)	79.5(2)
Pd–C(9)	1.997(4)	N(3)–Pd–C(9)	79.8(2)
O(1)–N(1)	1.246(6)	N(1)–Pd–C(9)	168.8(2)
O(2)–N(3)	1.226(5)	N(3)–Pd–C(2)	172.9(2)
N(1)–N(2)	1.301(7)	Pd–N(1)–O(1)	127.1(4)
N(2)–C(7)	1.464(6)	Pd–N93)–O(2)	128.5(3)
N(2)–C(1)	1.440(6)	Pd–N(1)–N(2)	114.8(3)
N(4)–C(8)	1.435(6)	Pd–N(3)–N(4)	114.8(3)
N(3)–N(4)	1.331(6)	Pd–C(2)–C(1)	113.5(3)
N(4)–C(14)	1.448(6)	Pd–C(9)–C(8)	114.0(3)
C(2)–C(1)	1.392(6)	Pd–C(2)–C(3)	130.7(4)
C(2)–C(3)	1.401(7)	Pd–C(9)–C(10)	130.0(4)
C(1)–C(6)	1.391(7)	N(1)–N(2)–C(1)	115.1(4)
C(3)–C(4)	1.382(7)	N(3)–N(4)–C(8)	114.6(4)
C(4)–C(5)	1.370(8)	N(2)–C(1)–C(2)	116.3(4)
C(5)–C(6)	1.380(7)	N(4)–C(8)–C(9)	116.5(4)
C(9)–C(8)	1.395(7)	N(2)–N(1)–O(1)	117.4(4)
C(9)–C(10)	1.415(7)	N(4)–N(3)–O(2)	116.6(4)
C(8)–C(13)	1.397(7)	N(2)–C(1)–C(6)	120.1(4)
C(10)–C(11)	1.395(7)	N(4)–C(8)–C(13)	119.8(4)
C(11)–C(12)	1.363(8)	N(1)–N(2)–C(7)	120.1(4)
C(12)–C(13)	1.380(7)	N(3)–N(4)–C(14)	120.4(4)
		C(1)–N(2)–C(7)	124.8(5)
		C(8)–N(4)–C(14)	124.9(4)

Table 7

Positional parameters with their estimated standard deviations

Atom	x	y	z	B (Å^2) [a]
Pd	0.12607(5)	0.24018(2)	0.47116(2)	2.800(5)
O(1)	0.1812(6)	−0.0010(3)	0.4154(2)	4.50(8)
O(2)	0.0840(6)	0.1910(3)	0.2878(2)	4.54(8)
N(1)	0.1558(6)	0.0645(3)	0.4755(2)	3.16(7)
N(2)	0.1753(5)	0.0226(3)	0.5506(2)	3.09(7)
N(3)	0.1070(5)	0.2629(3)	0.3424(2)	3.26(7)
N(4)	0.1085(6)	0.3708(3)	0.3174(2)	3.09(7)
C(1)	0.1406(7)	0.1011(3)	0.6179(2)	2.65(7)
C(2)	0.1108(6)	0.2139(3)	0.5950(2)	2.58(7)
C(3)	0.0573(7)	0.2864(4)	0.6600(3)	3.04(8)
C(4)	0.0468(6)	0.2488(4)	0.7419(3)	3.37(8)
C(5)	0.0850(8)	0.1382(4)	0.7626(3)	3.4(1)
C(6)	0.1304(8)	0.0622(4)	0.7000(3)	3.48(9)
C(7)	0.2228(8)	−0.0973(4)	0.5615(4)	4.0(1)
C(8)	0.1426(6)	0.4515(4)	0.3828(2)	2.70(7)
C(9)	0.1514(6)	0.4088(3)	0.4644(2)	2.80(8)
C(10)	0.1995(7)	0.4883(3)	0.5268(3)	3.28(9)
C(11)	0.2248(9)	0.6027(4)	0.5071(3)	3.9(1)
C(12)	0.2108(8)	0.6406(4)	0.4267(3)	3.8(1)
C(13)	0.1714(7)	0.5654(4)	0.3627(3)	3.3(1)
C(14)	0.0837(8)	0.3987(5)	0.2297(3)	4.2(1)

[a] Isotropic equivalent thermal parameters: $B_{eq} = \frac{1}{3} \cdot [a^2B(11) + b^2B(22) + c^2B(33)]$

lated nitrosoamine [Pd{(NO)N(CH_3)C_6H_4}Cl(PPh_3)], with P *trans* to N, and find an N=O separation of 1.243(18) Å.

Apart from the above details the structure of **5** can be considered as normal [21–24].

Experimental

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on AC-200 and WM-250 NMR spectrometers. IR spectra were recorded with CsI or CsBr pellets, unless otherwise specified, on a Perkin Elmer 883 instrument. Microanalyses and mass spectra were performed in the analytical laboratory of the ETH Zürich.

*Preparation of [Pd(μ-OAc)(ONN(CH_3)C_6H_4)]$_2$, Di-μ-acetato-bis(*N*-methyl-*N*-nitrosoaniline-C_2,NO(dipalladium(II).* A solution of Pd(OAc)$_2$ (1.12 g, 5.0 mmol) and *N*-methyl-*N*-nitrosoaniline (0.61 ml, 5.0 mmol) in 100 ml of HOAc was refluxed for 30 min. Removal of the solvent under vacuum was followed by recrystallization of the residue from CH_2Cl_2/pentane, to afford 1.42 g (91%) of product. The remaining complexes **4a**–**4e** were prepared analogously, and analytical and selected spectroscopic data are given in Tables 1 and 2.

*Preparation of **4f**.* (a) A solution of the μ-OAc complex, **4**, Y = H, (30 mg, 0.05 mmol) dissolved in 5 ml of acetone was treated with 1 ml of aqueous NaCl (20 mg,

Table 8

Experimental data for the X-ray diffraction study of **5**

Formula	$C_{14}H_{14}N_4O_2Pd$
Molecular weight	376.69
Crystal dimensions, mm	0.40×0.20×0.15
Data collection at T, °C	21
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	7.215(1)
b, Å	11.778(1)
c, Å	15.965(2)
V, Å^3	1356.7(5)
Z	4
ρ (calcd), g cm^{-3}	1.844
μ, cm^{-1}	13.582
Radiation	Mo-$K_{\bar{\alpha}}$, graphite monochromated
	$\lambda = 0.71069$ Å
Measured reflections	$+h, +k, +l$
θ range, deg	$2.20 \leq \theta \leq 27.0$
Scan type	$\omega/2\theta$
Scan width, deg	$1.10 + 0.35 \tan \theta$
Maximum counting time, s	65
Background time, s	0.5×scan time
Maximum scan speed, deg min^{-1}	10.5
Prescan rejection limit	0.55 (1.82 σ)
Prescan acceptance limit	0.025 (40 σ)
Horizontal receiving slit, mm	$1.90 + \tan \theta$
Vertical receiving slit, mm	4.00
Number of independent data collected	1717
Number of observed reflections (n_0) ($\|F_0\|^2 \geq 2.0\ \sigma\ (\|F\|^2)$)	1457
Number of parameters refined (n_v)	190
R	0.028
R_w	0.035
GOF	1.205

$R = \Sigma \| F_o | - 1/k | F_o \| / \Sigma | F_o |$
$R_w = [\Sigma w(| F_o | - (1/k) | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$, where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o^2) + f^2(F_o^4)]^{1/2}/2F_o$ with $f = 0.040$
GOF $= [\Sigma w(| F_o | - (1/k) | F_c |)^2 / (n_o - n_v)]^{1/2}$

0.3 mmol). A precipitate of the product was rapidly formed and was then filtered off and dried under vacuum to give 25.5 mg (92%) of the required product. (b) A solution of $PdCl_2$ (8.9 mg, 0.05 mmol), 2 ml of methanol and 6 μl (0.05 mmol) of *N*-methyl-*N*-nitrosoaniline was stirred at ambient temperature for 3 h, and the precipitate formed filtered off and dried: 12.5 mg (90%).

The bridge-splitting reactions involving pyridine, PPh_3 and diphos, $(Ph_2PCH_2-)_2$ were carried out as described in the literature [29]: For **9**, ^{31}P NMR, δ 42.2, 59.0, ^2J(P,P) = 31. ^{1}H NMR, δ 3.35, N–CH_3. For **10**: ^{31}P NMR, δ 21.1. ^{1}H NMR, δ 2.60, N–CH_3 7.16, H 3, 6.50, H 4, 6.68, H 5 and 6.25, H 6.

Preparation of 11. A suspension of the chloro complex **5f** (277 mg, 0.50 mmol) in 25 ml of acetonitrile was treated with 195 mg $AgBF_4$. Stirring for 0.5 h was followed by filtration and concentration of the solution to afford 385 mg (94%) of the crude, fairly insoluble; product. ^1H NMR (CD_3CN) δ 3.50, N–CH_3; 2.00 2 eq. CH_3CN ligands (presumably exchanged with solvent) ^{13}C NMR, δ 32.0 N–CH_3. 143.0, 137.2, C(1) or C(2), 134.9, 128.0, 126.2, 115.4.

Preparation of 7. A suspension of the chloro complex **4f** (27.7 mg, 0.05 mmol) in chloroform-*d* was treated with $Bu^tN{\equiv}C$ (34 μl, 0.30 mmol). Within 2 min a yellow-green solution had been formed and the NMR spectroscopy indicated that reaction was complete. The solvent was removed and the residual oil dried under vacuum, then triturated with pentane to afford a yellow-green solid. This solid appears to be air sensitive in that it slowly becomes pink and eventually violet without any significant change in its ^1H NMR spectrum. In solution at $-25\,^\circ C$ the complex decomposes during a few hours. Microanalysis data are listed in Table 1. ^{13}C NMR ($CDCl_3$), δ 153.8, 141.3, 137.3, 133.0, 132.2, 128.9 128.3, 127.0, aromatic carbons, 58.3 coordinated Me_3CNC; 57.1 inserted Me_3CNC; 37.4, N–CH_3; 31.1, inserted $(CH_3)_3CNC$; 29.9, $(CH_3)_3CNC$ coordinated. Molecular wt: 506.8 (526.4). IR (CsI pellet) 253 cm^{-1}, Pd–Cl; ($CHCl_3$ solution) 2333, 2204 cm^{-1} (C≡N) stretches; 1636, 1612 (C=N) (CsI pellet) 2200, 2220 cm^{-1}, (C≡N); 1637, 1620, 1610 cm^{-1} (C=N).

Reaction of 4f with methyl lithium. A solution of complex **4f** (40 mg, 0.072 mmol) and PPh_3 (75 mg, 0.29 mmol) in 5 ml of absolute C_6H_6 was stirred for 1 h, then MeLi (90 ml, 1.6 *M* (ether), 0.144 mmol) was added. The resulting suspension was stirred for 4 h then treated with 2 ml of water. Addition of ether gave three layers. Concentration of the ethereal layer and filtration gave ca. 8 mg of crude product which was a mixture containing mainly **10**.

A similar reaction of **4f** with phenyl lithium and n-butyl lithium gave **10** as the only identifiable product.

Synthesis of 12a. A solution of the cyclometallated phosphite (90 mg, 0.10 mmol) and PPh_3 (52 mg, 0.20 mmol) in 6 ml of C_6H_6 was treated with methyl lithium (1.25 ml 1.6 *M* (ether), 0.20 mmol) and the mixture stirred for 1 h at 5 °C. Addition of 0.5 ml of methanol was followed by concentration and recrystallization of the precipitate from benzene/hexane to afford 98 mg (70%) of product. Compounds **12b** and **12c** were prepared similarly except that water was used for the hydrolysis. δ ^{31}P NMR: 148.4 (phosphite), 28.3 (phosphine), ^2J(P, P) = 32 Hz. δ ^1H NMR. CH_3–Pd = 0.53 ^3J(phosphite-P, CH_3) = 9.8, ^3J(phosphine-P, CH_3) = 7.3. δ ^{13}C, CH_3, 11.5 ^2J(phosphite-P), CH_3) = 141, ^2J(phosphine-P), CH_3) = 11. Microanalysis calcd: C, 64.13; H, 4.65; found: C, 63.78; H, 4.51%. For **12c**: Microanalysis, calcd: C, 66.80, H, 5.21, found: C, 66.50; H, 5.22%.

Compounds **13** and **14** were prepared in the same way as the corresponding *N*-nitrosoderivatives. Spectroscopic data are given in Table 4.

Reactions with Me_4Sn. A solution of complex **4d** (1.2 g, 2.0 mmol) and 3 ml (20 mmol) of Me_4Sn in 50 ml of acetone was stirred for two days. The palladium metal was filtered off and the filtrate evaporated. The 'residue' was extracted with diethyl ether and the extract shaken with water to remove Me_3SnOAc, dried ($MgSO_4$) and evaporated to leave 475 mg (79%) of pure product. MS, $m/e = 150$, IR ν(N=O), 1440 cm^{-1}. For the 4-OCH_3 analog: MS, $m/e = 180$, IR, ν(N=O), 1438 cm^{-1}.

A solution of 12 mg (0.02 mmol) of **4d**, 30 μl of Me_4Sn (0.20 mmol) and 0.5 ml of

MeI in 1.5 ml acetone was stirred for 2 h then evaporated and the crude residue shown by ^{1}H NMR to consist of 65% of the methylated product, **6**, R = CH_3, and 35% of complex **4g**. When a stoichiometric amount of Me_4Sn and an excess of MeI was used, after 6 h there was ca. 70% conversion. Reactions involving $^{13}CH_3I$ and CD_3I (Stohler Isotopes) gave ca. 40 and 50% conversion, respectively.

Preparation of N-*methyl*-N-*nitroso-2-phenylethinyl-aniline.* A solution of complex **4d** (300 mg, 0.50 mmol) and diphos (800 mg, 2.0 mmol) in 20 ml of CH_2Cl_2 was treated with $Me_3SnC{\equiv}CPh$ (220 μl, 1.0 mmol) and the resulting solution stirred for 18 h. Evaporation left an oil, which was dissolved in ether and then treated with ca. 20 ml 6 *M* KF solution. The ether layer was separated, dried, and evaporated, to afford 120 mg (51%) of pure product. IR ν(C≡C), 2219 cm^{-1}; MS, $m/e = 236$ (molecular ion). Microanalysis calcd.: C, 76.27, H, 5.08; N, 11.86; found: C, 75.97; H, 5.21; N, 11.45%.

Reaction with $Bu^n_3SnCH{=}CH_2$. Complex **4d** (12 mg) was treated with 21 mg of PPh_3 in 2 ml of acetone-d_6 and the resulting solution treated with 12 μl $Bu^n_3SnCH{=}CH_2$. The progress of the reaction was monitored for 18 h in situ by ^{1}H NMR spectroscopy.

Reaction with $Bu^n_3SnCH_2CH{=}CH_2$. A suspension of complex **4f** (56 mg, 0.10 mmol) in 6 ml of CH_3CN was treated with $AgBF_4$ (39 mg, 0.20 mmol), to give a solution of complex **11**. The solution was filtered and $Bu^n_3SnCH{=}CH_2$ (36 μl, 0.20 mmol) was added. After 10 min the product 33 mg (44% based on Pd) was filtered off. The solvate complex $[Pd(\eta^3\text{-}C_3H_5)(CH_3CN)_2]BF_4$ was identified in the mother liquor by ^{1}H NMR spectroscopy.

X-Ray structure determination. Crystals suitable for X-ray determination were obtained by slow evaporation of a CH_2Cl_2 solution at $-20\,^\circ$C. They are air stable.

A prismatic crystal was chosen for the data collection and mounted on a glass fiber at a random orientation. An Enraf–Nonius CAD4 diffractometer was used for determination of the space group and cell constants and for the data collection. Cell constants were obtained by a least squares fit of 25 reflections ($8.7 < \theta < 17.1$) using the CAD4 centering routines. Crystal data and experimental details are summarized in Table 8. Data were collected at variable scan speed to obtain constant statistical precision on the measured intensities. Three standard reflections ($\bar{1}$ 2 7, $\bar{1}$ $\bar{1}$ 6, 1 1 $\bar{6}$) were measured every hour to check the stability of the crystal and of the experimental conditions, and no significant variation was detected. The crystal orientation was checked by measuring three standard reflections ($\bar{2}$ 3 4, $\bar{1}$ $\bar{3}$ 5, 5 1 7) after every 300 reflections. Data were corrected for Lorentz and polarization and for absorption using the azimuthal (ψ) scans of 4 reflections at high χ angles ($\chi \geq 86.0$): $\bar{3}$ 1 $\bar{3}$, $\bar{4}$ 1 $\bar{3}$, $\bar{5}$ 1 $\bar{5}$, $\bar{6}$ 1 $\bar{6}$. Transmission factors were in the range 0.998–0.955. The standard deviations for the intensities were calculated in terms of statistics alone. Reflections having $F_o \geq 2.0\sigma(F_o)$ were considered as observed, while value F_0^2 of 0.0 was given to those reflections having negative net intensities. The structure was solved by standard Patterson and Fourier methods and refined by full matrix least-squares by minimization of the function $\Sigma[w(F_o - (1/k)F_c)^2]$ with $w = [\sigma^2(F_o)]^{-1}$. Anisotropic temperature factors were used for all atoms except hydrogens; these were included in the calculated positions (C–H = 0.95 Å, $B_{iso} = 5.0$ Å^2) but not refined. Scattering factors were taken from ref. 30 and corrected for the real and imaginary part of the anomalous dispersion [30]. No extinction correction was deemed necessary. Upon convergence (no shift to error ratio > 0.02) the final Fourier difference

map showed no significant features. All calculations were carried out with the SDP crystallographic programs [31]. The handedness of the crystal was tested by refining the two possible sets of coordinates and comparing the R_w agreement factors. The coordinates corresponding to the lowest R_w, value with the equivalent thermal parameter, are given in Table 4. A complete table of bond lengths and angles, a table of thermal parameters, and a list of observed and calculated structure factors are available from the authors.

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