Reactions of Cyclopalladated Compounds. Part 24.[1],† Reactivity of the Pd–C Bond of Cyclopalladated Compounds towards Isocyanides and Carbon Monoxide. Role of the Donor Group

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The Pd–C bond of a series of cyclopalladated compounds of general formula $[Pd_2(C\ldots SMe)_2(\mu\text{-}Cl)_2]$, obtained through direct palladation of thioether ligands, is remarkably reactive towards insertion of one isocyanide as compared to the corresponding compounds in which the SMe unit has been replaced by a NMe_2 moiety. The most reactive compound of the series is that derived from orthopalladation of benzyl methyl thioether, which leads either to chloride-bridged dimers with benzyl- or phenyl-isocyanide or to imino-bridged dimers with t-butyl isocyanide. With the other cyclopalladated compounds, insertion of the isocyanides also takes place in the presence of 2 equivalents of isocyanides per palladium atom though less readily as in the previous case, affording new imino units σ-bonded to palladium *via* their imino carbon atom. Carbon monoxide is readily inserted into the Pd-C bond of most of these cyclopalladated compounds to afford new palladated acyl groups, this reaction being reversible.

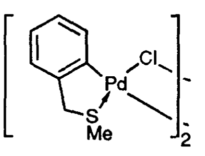
The insertion of carbon monoxide into metal–carbon bonds, which is somehow relevant to the Fisher–Tropsh synthesis, has been extensively studied in organometallic chemistry and in homogeneous catalysis.[2] Accordingly the reaction of organometallic compounds with isocyanides is also very popular among organometallic chemists[3] since it allows an easy way to the formation of C–C bonds and may also shed some light on the mechanism of the carbonylation reactions. Much insight into these potentially economically useful reactions can be gained by studying the reaction between CO or RNC and organometallic compounds obtained *via* direct metallation of aryl or alkyl groups through the C–H activation reaction. Indeed, the reaction of CO with cyclometallated compounds has been widely investigated so far particularly for those compounds derived from the palladation of tertiary amines[4] whereas the related reaction with isocyanides has been less extensively examined.[5]

During the previous studies of this group on the reactivity of cyclopalladated compounds[6] it appeared that the nature of the donor atom of these species is of crucial importance. When we started this work no information was available about the insertion of CO or RNC into the M–C bonds of cyclometallated compounds in which the donor atom is sulphur. In order to obtain some insight into this area we have now studied the reactivity of compounds (1)—(6)[7] towards isocyanides and carbon monoxide. Moreover, to understand better the role of the donor group upon the reactivity of the Pd–C bond, the behaviour of these compounds will be compared with those of their nitrogen-containing counterparts. Some aspects of the present work have appeared in a preliminary communication.[8]

Results

Reactions with Isocyanides.—The most reactive of the cyclopalladated complexes (1)—(6) is undoubtedly (1). The reactions performed on this compound are summarized in Scheme 1.

When (1) is treated with slightly less than 2 equivalents of t-butyl isocyanide [reaction (*i*)] it was possible to observe the formation of the monomeric compound (7) in which the isocyanide is simply co-ordinated to the palladium centre *via* its carbon atom [ν(C≡N) 2 209 cm^{-1}]. In a typical experiment 0.9 equivalent of Bu^{t}NC was added to 0.5 equivalent of (1). This led to the formation of 0.9 equivalent of (7) together with 0.05 equivalent of unreacted (1), no insertion product (8) (see later) being detected after less than 10 min. This suggests that the insertion of isocyanide into the Pd–C bond of complex (1) is significantly slower than the chloride-bridge splitting reaction and cannot compete with it. It is most likely that in (7) (as well as in the other monomeric compounds described in this paper) the termimal isocyanide ligand is co-ordinated *cis* to the σ-bonded carbon of the chelate as for most of the related monomers obtained by cleavage of chloride bridges. Compound (7) however was not stable in solution and rearranged in solution over *ca.* 10 h at room temperature to the new dimeric imino-bridged complex (8) [reaction (*ii*)]. When compound (1) is treated with slightly more than 2 equivalents of isocyanide



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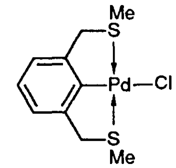

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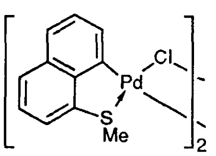

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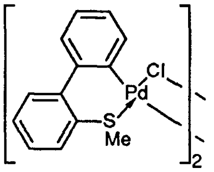

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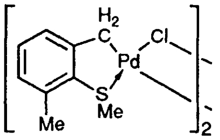

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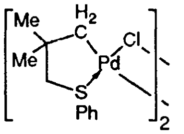

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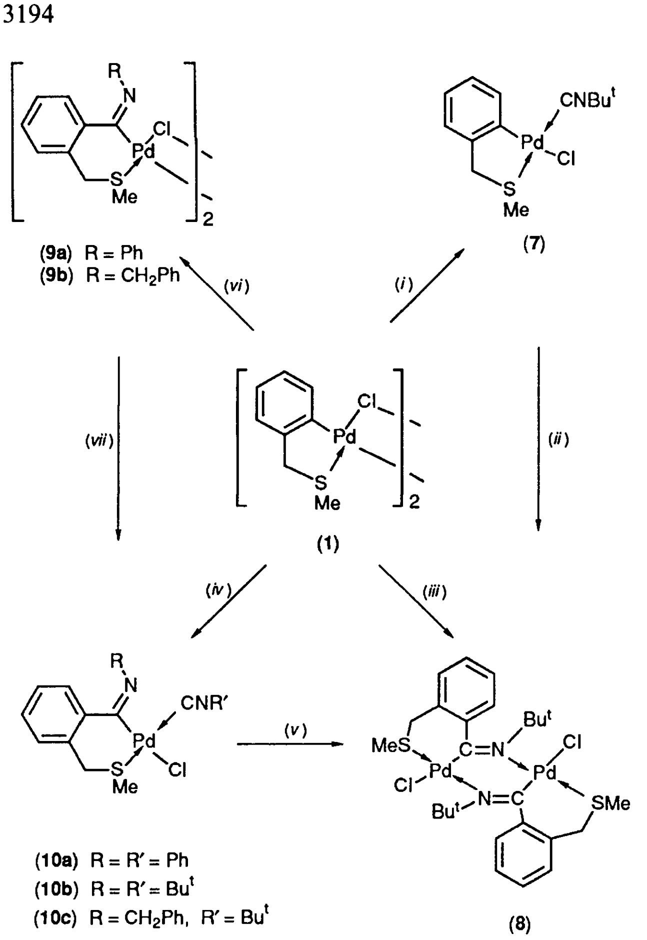
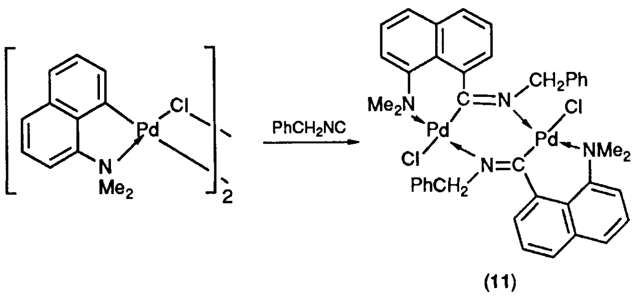
† Taken in part from the Ph.D. thesis of J. Dupont, Université Louis Pasteur, Strasbourg, 1988.



Scheme 1. Reaction conditions and reagents: All reactions were performed in CH_2Cl_2 at 20 °C. (*i*) $[Bu^tNC]/[(\mathbf{1})] < 2:1$; (*ii*) 10 h; (*iii*) $[Bu^tNC]/[(\mathbf{1})] > 2:1$; (*iv*) $[RNC]/[(\mathbf{1})] > 4:1$; (*v*) $R = R' = Bu^t$, 48 h; (*vi*) $[RNC]/[(\mathbf{1})] > 2:1$; (*vii*) $[R'NC]/[(\mathbf{9})] = 2:1$

[reaction (*iii*)] the excess of isocyanide catalyses the transformation of (**7**) into (**8**).

Compound (**8**) was formed either directly by reaction (*iii*) or by slow rearrangement of (**10b**) [reaction (*v*)], which could be obtained only by adding a large excess of t-butyl isocyanide to (**1**) [reaction (*iv*)]. The structure of complex (**8**) has been determined by a *X*-ray crystallographic study.[8] Surprisingly the formation of compound (**8**) was irreversible and (**8**) was found to be completely inert to bridge-splitting reactions with pyridines or phosphines. A similar behaviour has been observed for related doubly bridged compounds with imino units[9] though in this case cleavage of the bridges was observed with excess of RNC. At present the formation of (**8**) from (**1**) cannot be rationalized since this type of imino-bridged compound is not formed in reactions of other related complexes studied so far with various isocyanides. Nevertheless it is noteworthy that the reaction of excess of benzyl isocyanide with bis (8-dimethylaminonapthyl)dipalladium dichloride leads almost quantitatively to compound (**11**) as deep red crystals. Analytical and spectroscopic data show that one benzyl isocyanide unit has been inserted into the Pd–C bond of the starting compound, and thus (**11**) to be a dimeric molecule. Since, like compound (**8**), it is completely inert to bridge-splitting reactions it is likely to be bridged by imino rather than chloride groups between two palladium atoms. This may explain the deep red colour of this compound which is similar to that of (**8**). All other dimeric chloride-bridged compounds studied in this paper are pale yellow or white.

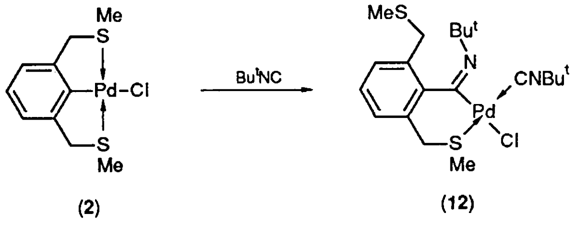


(**11**)

The reactions between complex (**1**) and phenyl- or benzyl-isocyanide show trends similar to those found for t-butyl isocyanide. For example, when (**1**) was treated with slightly more than 2 equivalents of these isocyanides the instantaneous formation of the inserted products (**9a**) and (**9b**) [reaction (*vi*)] was observed. We believe that these two compounds are chloride-rather than imino-bridged species for the following reasons: they are both pale yellow and they do react with another equivalent of RNC to afford the monomers (**10a**) and (**10c**) respectively [reaction (*vii*)]. This latter reaction, however, was much slower than the other bridge-splitting reactions [*e.g.* (*i*)] and quantitative formation of (**10a**) and (**10c**) was only reached after *ca.* 1 h. In contrast to (**10b**), compounds (**10a**) and (**10c**) were indefinitely stable both in solution and in the solid state. In presence of (**1**), compound (**10a**) afforded the dimer (**9a**), thus emphasizing the relatively weak interaction between the palladium centre and the terminally bonded PhNC unit in (**10a**).

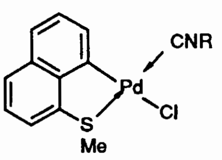
This rapid insertion under mild conditions of isocyanides into the Pd–C bond of compound (**1**) is markedly different from the behaviour found earlier for an analogous compound, in which the SMe unit is replaced by a NMe_2 group, where insertion reactions usually required high temperatures and/or large excesses of isocyanide reagents.[5e]

No reaction occured when complex (**2**) was treated with 1 equivalent of RNC. However, in the presence of an excess of t-butyl isocyanide ($[Bu^tNC]/[Pd] > 2:1$) the insertion of this isocyanide into the Pd–C bond of (**2**) was observed after *ca.* 2h in dichloromethane at room temperature to give compound (**12**) in good yields. The reactivity of the aryl unit σ-bonded to the palladium atom in (**2**) is therefore markedly lower than that of this unit in related (**1**). This is obviously due to the chelating effect of the two SMe groups that prevent the migration of the aryl C atom on a RNC unit co-ordinated to Pd in its apical position (see later). This rection of (**2**), though slow, emphasized however a marked improved reactivity of the Pd–C bond in this compound over that in the corresponding compound in which the SMe units are replaced by NMe_2 groups. So far no reaction has been detected at the Pd–C bond of $[Pd\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}Cl]$ with either carbon monoxide or isocyanide reagents.[10]

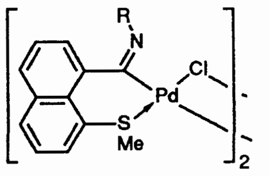


(**2**) (**12**)

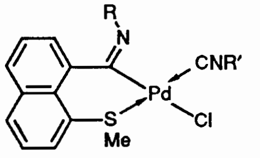
The behaviour of complex (**3**) towards isocyanides differs from that of (**1**) in many respects. With stoicheiometric amounts of RNC (R = Ph, CH_2Ph, or Bu^t) cleavage of the chloride bridges readily took place affording the monomeric complexes (**13**) which have been fully characterized by their analytical and spectroscopic data (see Tables 1 and 2). In marked contrast to (**7**) these monomers were indefinitely stable in solution at room temperature. They did however afford the inserted dimeric complexes (**14**) when heated in refluxing chlorobenzene for *ca.* 15 min. Note however that no insertion reaction took place with (**13c**) even when refluxed in chlorobenzene for 2h. The chloride-bridge splitting reactions of these dimers are much easier than those of the related compounds (**9a**) and (**9b**) since monomers (**12a**) and (**12c**) were formed almost instantaneously by treating (**14a**) with 1 equivalent of isocyanide.



(13a) R = Ph
(13b) R = CH_2Ph
(13c) R = Bu^t

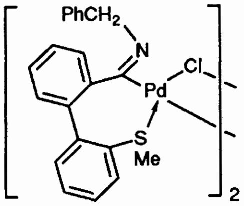


(14a) R = Ph
(14b) R = CH_2Ph



(15a) R = R' = Ph
(15b) R = R' = Bu^t
(15c) R = Ph, R' = Bu^t

When compound (**13c**) was treated with a 0.5 equivalent of t-butyl isocyanide this led to a mixture of (**13c**) and (**15b**) (1:1 ratio). This result clearly indicates that (**13c**) does react in a stoicheiometric way with RNC in contrast to the catalytic reaction that was found in the case of compound (**7**). It is also interesting that adding equimolar amounts of phenyl isocyanide to (**13c**) afforded the same compound (**15c**) as that obtained through the reaction of (**13a**) with t-butyl isocyanide. This emphasizes the higher reactivity of phenyl isocyanide *vs.* t-butyl isocyanide in these reactions, in accord with previous related studies.[5e]



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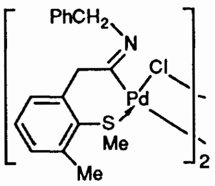

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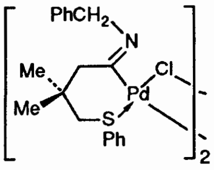
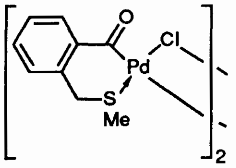


(18)

The behaviour of the other sulphur-containing cyclopalladated compounds, *e.g.* (**4**)—(**6**), towards isocyanides is analogous to that observed for compound (**3**), affording for example with 1 equivalent of benzyl isocyanide at high temperature the chloride-bridged dimers (**16**)—(**18**) containing an imino group σ-bonded to Pd.

Reactions with Carbon Monoxide.—When carbon monoxide was passed through a suspension of complex (**1**) in dichloromethane at room temperature a pale yellow solution was formed after *ca.* 1—3 min, from which (**19**) precipitated (after *ca.* 2 h) as a solid insoluble in common organic solvents. The initial dissolution of the product is probably a consequence of the chloride-bridge splitting reaction affording a monomeric compound through co-ordination of the CO, which is then followed by the slow formation of (**19**). Whereas no reaction was observed between (**2**) and carbon monoxide, compound (**3**) reacts in a similar manner to (**1**) to yield the six-membered palladocycle (**20**).



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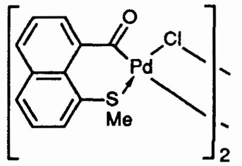


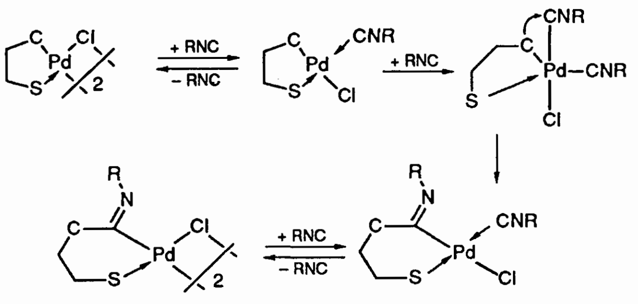
(20)

The insertion of CO into the Pd–C bond of complexes (**1**) and (**3**) is a reversible reaction, since upon heating (**19**) and (**20**) at 35 °C in dichloromethane the starting materials (**1**) and (**3**) were regenerated quantitatively. This insertion–deinsertion of CO could be repeated several times with no decomposition products being detected. Whereas compounds (**2**) and (**5**) do not exhibit any reaction with CO, the other palladocycles (**4**) and (**6**) display also a reversible CO insertion similar to that of (**1**) and (**3**), affording the acyl compounds (**21**) and (**22**) respectively (see Tables 1 and 2).

Discussion

The results we have found can be rationalized according to earlier work on related insertion reactions of isocyanides into the M–C bond of complexes of Pd or Pt. Indeed, several detailed studies have been performed in this area in order to understand how various factors can influence these reactions.[11] It has thus been established that in square-planar complexes of Pd or Pt, σ-bonded R groups can experience an intramolecular migration to either *cis* adjacent co-ordinated isocyanide or CO groups. It was also shown that the insertion can occur *via* an associative mechanism, as for the reaction of RNC with $[Pd(X)R'(PPh_3)_2]$. This process involves, as an important intermediate, the formation of a five-co-ordinated species from which the σ-bonded R' group migrates to a *cis* adjacent isocyanide to afford the insertion product.[11a]

The reactions observed in this study may occur *via* a similar associative process (Scheme 2). It is reasonable to assume that the deco-ordination of the sulphur atom in these palladocycles is not essential for the migration to take place. This is in agreement with what was reported earlier for the related reaction of $[\{Pd[C_6H_4(CH_2NMe_2)\text{-}2](\mu\text{-}Cl)\}_2]$ with Bu^tNC.[5e] In this case,



Scheme 2.

Table 1. Infrared and microanalytical data and colours of compounds **(8)**—**(22)**

	I.r. data (cm^{-1})[a]		Analysis(%)[b]			
Compound	ν(C=N)	ν(C≡N)	C	H	N	Colour
(8)	1 670		43.00	4.90	3.65	Red
			(43.10)	(5.00)	(3.85)	
(9a)·$0.5CH_2Cl_2$	1 565		45.05	3.80	3.30	Yellow
			(45.40)	(3.60)	(3.45)	
(9b)	1 580		48.15	3.90	3.65	Yellow
			(48.50)	(4.05)	(3.55)	
(10a)·$0.25CH_2Cl_2$	1 588	2 192	52.90	4.25	5.55	Pale yellow
	1 612		(52.75)	(3.90)	(5.55)	
(10b)	1 648	2 185	48.70	6.00	6.20	White
	1 628		(48.55)	(6.10)	(6.30)	
(10c)	1 578	2 200	53.20	5.10	5.60	White
			(52.75)	(5.05)	(5.85)	
(11)	1 559		56.05	4.60	6.30	Red
			(55.95)	(4.45)	(6.55)	
(12)	1 647	2 199	46.60	5.90	5.00	Pale yellow
			(47.55)	(6.15)	(5.55)	
(13a)		2 192	51.60	3.90	3.45	White
			(51.70)	(3.35)	(3.35)	
(13b)		2 208	53.05	3.70	3.30	White
			(52.80)	(3.75)	(3.25)	
(13c)		2 200	48.25	4.45	3.60	White
			(48.25)	(4.55)	(3.50)	
(14a)	1 532		51.40	3.50	3.20	Yellow
			(51.70)	(3.35)	(3.35)	
(14b)	1 549		52.80	3.80	3.05	Yellow
			(52.80)	(3.75)	(3.25)	
(15a)	1 650	2 200	57.80	4.00	5.60	Pale yellow
			(57.60)	(3.65)	(5.35)	
(15b)	1 645	2 195	52.10	5.70	5.70	White
			(52.40)	(5.65)	(5.80)	
(15c)	1 582	2 203	55.40	4.55	5.55	White
	1 605		(55.10)	(4.60)	(5.60)	
(16)	1 570		54.95	3.85	3.05	Yellow
			(55.05)	(3.95)	(3.05)	
(17)	1 582		50.25	4.80	3.60	Yellow
	1 546		(49.75)	(4.40)	(3.40)	
(18)	1 570		51.65	4.95	3.15	Pale yellow
			(52.05)	(5.05)	(3.20)	
(19)	1 660[c]		35.05	3.00		Yellow
			(35.20)	(2.95)		
(20)	1 670[c]		41.65	2.60		Yellow
			(42.00)	(2.65)		
(21)	1 675[c]		47.80	3.30		White
			(47.60)	(3.15)		
(22)	1 690[c]		41.40	4.70		Yellow
			(41.30)	(4.35)		

[a] KBr pellets. [b] Calculated values in parentheses. [c] ν(C=O).

the deco-ordination of the NMe_2 group was not observed even in the presence of an excess of isocyanide [note however that the migration of the palladated aryl group of compound **(2)** onto a *cis* co-ordinated isocyanide could not occur if the deco-ordination of one of the sulphur atoms has not taken place so as to permit co-ordination of the isocyanide to the Pd atom]. In several reactions a second equivalent of isocyanide had to be added in order for the insertion to take place. In other instances we observed an apparent rearrangement of the monomeric compounds, usually at high temperature, to afford a dimeric compound containing an imino group. It is most likely that these latter reactions proceed also through the same general reaction path: upon heating the terminal isocyanide may be deco-ordinated (note that it was observed in many instances throughout this study that the isocyanide ligands are weakly bonded to Pd *trans* to the σ-bonded carbon atom) and thus react with the monomeric species still present in solution according to Scheme 2. It is indeed not likely in these monomers having only one isocyanide per Pd atom that the σ-bonded carbon of the palladated thioether ligand is able to migrate to the co-ordinated isocyanide within the co-ordination plane of Pd, since this would involve the concomitant deco-ordination of the S atom. The difference in behaviour between the compounds studied here might be assigned to the different *trans* effects exerted by the sulphur atoms in these complexes on the terminal isocyanide. In order to explain the observed results this effect should be strongest for the compound containing the benzyl methyl sulphide chelate since it is for this ligand that the insertion proceeds the better. However, an additional important *cis* effect should also be operative in order to explain the high reactivity of the palladated carbon atom towards migration to the co-ordinated isocyanides. This is even more apparent when comparing the reactivity of the corresponding compounds in which the SMe group is replaced by a NMe_2 unit and for which

Table 2. Proton n.m.r. data for compounds (**8**)—(**22**)

Compound	δ(J in Hz)^a
(**8**)	7.30—7.18 (m, 4 H, aromatic), 3.36 and 3.06 (2 d, 2 H, CH$_2$SMe, $^2J_{HH}$ = 11.8), 3.01 (s, 3 H, SMe), 1.43 (s, 9 H, Bu^t)
(**9a**)	7.24—6.79 (m, 9 H, aromatic), 4.02 and 3.57 (2 m, 2 H, CH$_2$SMe), 3.15, 2.38, and 2.35 (3 s, 3 H, SMe)
(**9b**)	7.20 and 6.30 (2 m, 9 H, aromatic), 4.75, 4.60, 4.25, and 3.40 (4 m, 4 H, CH$_2$), 3.08, 2.25, and 2.22 (3 s, 3 H, SMe)
(**10a**)	7.23—6.97 (m, 14 H, aromatic), 3.15 (br s, CH$_2$SMe), 1.60 (s, 3 H, SMe)
(**10b**)	7.31—6.87 (m, 4 H, aromatic), 3.16 (q, 2 H, CH$_2$SMe, $^2J_{HH}$ = 13.1), 2.50 (s, 3 H, SMe), 1.58 and 1.49 (2 s, 18 H, Bu^t)
(**10c**)	7.40—7.10 (m, 9 H, aromatic), 5.12 (s, 2 H, CH$_2$Ph), 3.28 (s, 2 H, CH$_2$SMe), 2.43 (s, 3 H, SMe), 1.36 (s, 9 H, Bu^t)
	^{b} 7.39—7.07 (m, 9 H, aromatic), 5.03 (q, 2 H, CH$_2$Ph, $^2J_{HH}$ = 14.8), 3.26 (q, 2 H, CH$_2$SMe, $^2J_{HH}$ = 14.0), 2.33 (s, 3 H, SMe), 1.27 (s, 9 H, Bu^t)
(**11**)	8.01—6.75 (m, 11 H, aromatic), 5.39 and 4.78 (2 d, 2 H, CH$_2$Ph, $^2J_{HH}$ = 15.0), 3.75 and 3.29 (2 s, 6 H, NMe$_2$)
(**12**)	7.40 and 6.98 (2 d, 2 H, aromatic), 7.11 (t, 1 H, aromatic), 3.70 and 3.48 (2 d, 2 H, CH$_2$SMe, $^2J_{HH}$ = 14.1), 3.37 and 3.14 (2 d, 2 H, CH$_2$SMe, $^2J_{HH}$ = 13.5), 2.47 and 2.05 (2 s, 6 H, SMe), 1.60 and 1.51 (2 s, 18 H, Bu^t)
(**13a**)	7.81—7.18 (m, 11 H, aromatic), 3.05 (s, 3 H, SMe)
(**13b**)	7.77—7.08 (m, 11 H, aromatic), 5.02 (s, 2 H, CH$_2$Ph), 3.01 (s, 3 H, SMe)
(**13c**)	7.75 and 7.46 (2 m, 6 H, aromatic), 3.01 (s, 3 H, SMe), 1.66 (s, 9 H, Bu^t)
(**14a**)	8.18—6.63 (m, 11 H, aromatic), 3.14 (s, 3 H, SMe)
(**14b**)	8.11—6.78 (m, 11 H, aromatic), 5.19 and 4.63 (2 d, 2 H, CH$_2$Ph, $^2J_{HH}$ = 14.1), 2.97 (s, 3 H, SMe)
(**15a**)	7.84—6.87 (m, 16 H, aromatic), 2.86 (br s, 3 H, SMe)
(**15b**)	7.81—7.18 (m, 6 H, aromatic), 2.89 (br s, 3 H, SMe), 1.71 and 1.42 (2 s, 18 H, Bu^t)
(**15c**)	7.99—7.18 (m, 11 H, aromatic), 2.83 (br s, 3 H, SMe), 1.20 (s, 9 H, Bu^t)
(**16**)	7.69—6.98 (m, 12 H, aromatic), 5.09 (dd, 1 H, aromatic, $^2J_{HH}$ = 8.1, $^3J_{HH}$ = 1.1), 4.18 and 3.88 (2 d, 2 H, CH$_2$Ph, $^2J_{HH}$ = 11.9), 2.50 (s, 3 H, SMe)
(**17**)	7.66—6.94 (m, 8 H, aromatic), 4.71 (q, 2 H, CH$_2$Ph, $^2J_{HH}$ = 12.5), 3.71 and 3.04 (2 d, 2 H, CH$_2$C=N, $^2J_{HH}$ = 13.8), 2.67 (s, 3 H, SMe), 2.55 (s, 3 H, Me)
(**18**)	8.26—7.09 (m, 10 H, aromatic), 4.93 and 4.74 (2 d, 2 H, CH$_2$Ph, $^2J_{HH}$ = 12.9), 2.63 (q, 2 H, CH$_2$C=N, $^2J_{HH}$ = 12.6), 2.28 and 1.31 (2 d, 2 H, CH$_2$SPh, $^2J_{HH}$ = 14.5), 1.00 and 0.73 (2 s, 6 H, CMe$_2$)
(**19**)^c	7.33—6.81 (m, 4 H, aromatic), 3.47 (s, 2 H, CH$_2$S), 2.58 (s, 3 H, SMe)
	^{b} 7.39—6.90 (m, 4 H, aromatic), 3.39 (q, 2 H, CH$_2$S, $^2J_{HH}$ = 13.8), 2.62 (s, 3 H, SMe)
(**20**)^d	8.06—7.41 (m, 6 H, aromatic), 2.63 (br s, 3 H, SMe)
(**21**)^d	7.64—6.85 (m, 8 H, aromatic), 2.60 (s, 3 H, SMe)
(**22**)	7.88 and 7.34 (2 m, 5 H, aromatic), 3.07 (s, 2 H, CH$_2$CO), 2.41 (s, 2 H, CH$_2$SPh), 0.91 (s, 6 H, CMe$_2$)

^{a} In CDCl$_3$ at 293 K; s = singlet, d = doublet, q = quartet, m = multiplet, and br = broad. ^{b} At 193 K. ^{c} In CD$_2$Cl$_2$ + εC$_5$D$_5$N$_5$. ^{d} In CDCl$_3$ + εC$_5$D$_5$N$_5$ (ε < 1%).

the rate of *cis* migration to co-ordinated RNC reagents is often very low or impossible to achieve.

Conclusion

The Pd–C bonds of the cyclopalladated thioether complexes are remarkably reactive towards the 'insertion' of isocyanides and carbon monoxide. The rate of these reactions is much faster than the reactions of their nitrogen-containing analogues. According to previous related work in this area this suggests that the palladated carbon atoms of the new compounds studied herein display an increased nucleophilicity as compared to those of their nitrogen-containing analogues.[11]

Experimental

General.—Unless otherwise specified the reactions were routinely carried out using Schlenk techniques under an atmosphere of pure dry nitrogen and using dry oxygen-free solvents. Infrared spectra were recorded as KBr pellets in the region 4 000—400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer, ^{1}H n.m.r. spectra at 200.13 and 400.26 MHz using Bruker SY200 and AM400 instruments respectively. Proton chemical shifts are positive downfield relative to external SiMe$_4$. Elemental analyses were carried out by the Service Central de Microanalyses du CNRS (France).

Syntheses.—Compounds (**1**)—(**3**), bis(8-dimethylaminonaphthyl)dipalladium dichloride,[12] and phenyl isocyanide[13] were prepared according to the procedures described in the literature. All other reagents were obtained from commercial sources and were used as received without further purification. Analytical and spectroscopic data for the compounds are given in Tables 1 and 2 respectively.

Compound (**7**). A solution of t-butyl isocyanide (0.038 g, 0.48 mmol) in dichloromethane (5 cm^3) was added to a suspension of complex (**1**) (0.14 g, 0.25 mmol) in dichloromethane (5 cm^3), affording immediately a light yellow solution. Concentration of this solution to *ca.* 3 cm^3 under reduced pressure and addition of hexane (25 cm^3) led to the formation of a light yellow solid which was collected by filtration, washed with hexane (3 × 15 cm^3), and dried *in vacuo*. Due to the stoicheiometry required for the reaction, contamination of (**7**) by some starting material could not be avoided and thus no reasonable analyses could be obtained for this compound.

Compound (**9b**). A solution of benzyl isocyanide (0.12 g, 1 mmol) in dichloromethane (15 cm^3) was added to a stirred suspension of complex (**1**) (0.27 g, 0.48 mmol) in dichloromethane (15 cm^3) at room temperature and the reaction mixture was stirred for 0.2 h. The yellow-orange solution thus obtained was concentrated to *ca.* 5 cm^3 under reduced pressure. Addition of hexane (50 cm^3) led to the formation of (**9b**) as a yellow solid which was collected by filtration, washed with hexane (3 × 15 cm^3), and dried *in vacuo* (0.37 g, 98%).

Complexes (**8**) and (**9a**) were prepared in almost quantitative yield using a similar procedure.

Compound (**10b**). To a stirred suspension of complex (**1**) (0.28 g, 0.5 mmol) in dichloromethane (25 cm^3) a large excess of t-butyl isocyanide (0.2 g, 2.5 mmol) was quickly added and the reaction mixture was stirred at room temperature for *ca.* 0.2 h. The light yellow solution thus obtained was concentrated to *ca.* 5 cm^3 under reduced pressure and hexane (30 cm^3) was added. The white precipitate formed was collected by filtration, washed with hexane (3 × 20 cm^3), and dried *in vacuo* (0.36 g, 79%).

A similar procedure was used to prepare quantitatively compound (**10a**) using phenyl isocyanide.

Compound (**10c**). To a yellow solution of complex (**9b**) (0.16 g, 0.2 mmol) in dichloromethane (10 cm^3) t-butyl isocyanide (0.05 g, 0.6 mmol) in dichloromethane (5 cm^3) was added. After stirring at room temperature for 0.9 h the light yellow solution thus formed was concentrated to *ca.* 4 cm^3 under reduced pressure. Addition of hexane (25 cm^3) afforded compound (**10c**) as a white solid which was collected by filtration, washed with hexane (3 × 15 cm^3), and dried *in vacuo* (0.18 g, 91%).

Compound (**11**). To a yellow suspension of bis(8-dimethylamino-1-naphthyl)dipalladium dichloride (0.31 g, 0.5 mmol) in dichloromethane (30 cm^3) was added a large excess of benzyl isocyanide (0.36 g, 3 mmol). The red solution thus obtained was stirred at room temperature for 0.5 h, evaporated to dryness, washed with hexane (4 × 20 cm^3), diethyl ether (4 × 20 cm^3), and then dried *in vacuo*. Recrystallization from dichloromethane–hexane afforded compound (**11**) as dark red crystals (0.32 g, 74%).

Compound (**12**). To a yellow solution of complex (**2**) (0.24 g, 0.7 mmol) in dichloromethane (20 cm^3), t-butyl isocyanide (0.16 g, 2 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure and the residue was washed with hexane (3 × 25 cm^3), diethyl ether (3 × 25 cm^3), and dried *in vacuo*. The white-yellow solid thus obtained was redissolved in dichloromethane (3 cm^3) and hexane (40 cm^3) was added to give compound (**12**) as a white-yellow solid which was collected by filtration, washed with hexane (3 × 25 cm^3), and dried *in vacuo* (0.28 g, 85%).

The same procedure was used to prepare in almost quantitative yield compounds (**15a**) and (**15b**), starting from (**3**) and the appropriate isocyanides.

Compound (**13c**). To a suspension of complex (**3**) (0.31 g, 0.5 mmol) in dichloromethane (20 cm^3) was added t-butyl isocyanide (0.04 g, 0.5 mmol), giving immediately a colourless solution which was concentrated to *ca.* 4 cm^3. Addition of hexane (25 cm^3) led to the formation of a light yellow solid which was collected by filtration, washed with hexane (3 × 10 cm^3), and dried *in vacuo* (0.34 g, 96%).

A similar procedure was used to prepare compounds (**13a**) and (**13b**) using the appropriate isocyanide. The yields in both cases were almost quantitative.

Compound (**14b**). A light yellow solution of compound (**13b**) (0.21 g, 0.5 mmol) in chlorobenzene (35 cm^3) was heated at reflux for *ca.* 0.25 h. The orange-yellow solution thus obtained was concentrated to *ca.* 4 cm^3 under reduced pressure. Addition of hexane (30 cm^3) led to the formation of compound (**14b**) as a yellow solid which was collected by filtration, washed with hexane (3 × 10 cm^3), and dried *in vacuo* (0.20 g, 95%).

A similar procedure was used to prepare compound (**14a**) in 91% yield starting from the monomeric complex (**13a**). Compounds (**16**)—(**18**) were prepared in the same way and with comparable yields as (**14b**) starting from the corresponding compounds (**4**)—(**6**) to which 1 equivalent of benzyl isocyanide per palladium atom was added.

Compound (**15c**). Phenyl isocyanide (0.05 g, 0.5 mmol) in dichloromethane (7 cm^3) was added to a light yellow solution of complex (**13c**) (0.2 g, 0.5 mmol) in dichloromethane (10 cm^3) and the reaction mixture was stirred at room temperature for *ca.* 0.2 h. Concentration of this solution to *ca.* 4 cm^3 under reduced pressure and addition of hexane (30 cm^3) led to the formation of a white solid. This was collected by filtration, washed with hexane, and dried *in vacuo* (0.21 g, 84%).

Compound (**19**). Carbon monoxide was bubbled through a suspension of complex (**1**) (0.3 g, 0.54 mmol) in dichloromethane (20 cm^3) affording after *ca.* 10 min a yellow solution. The reaction mixture was stirred for *ca.* 2.5 h at room temperature under carbon monoxide, during which time a yellow precipitate of compound (**19**) was formed; it was collected by filtration, washed with hexane (2 × 10 cm^3), and dried *in vacuo* (0.28 g, 85%).

A similar procedure was used to synthesize compounds (**20**), (**21**), and (**22**) from (**3**), (**4**), and (**6**) respectively with yields comparable to those obtained for (**19**).

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