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Preliminary communication

Substituent effects on carbene formation in isocyanide complexes of palladium(II)

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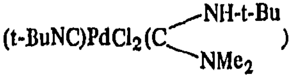
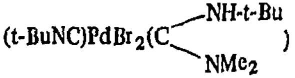
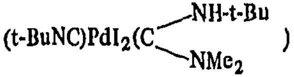
The reactions of the isocyanide complexes of the Ni–Pd–Pt group of metals are diverse, and include for example, insertion[1,2], dealkylation[3], substitution[4] and the formation of carbene-type derivatives[4–7]. However, the important factors influencing such reactivity have not been discussed, and we now report a series of new carbene complexes derived from Pd^{II} which illuminate this point.

Thus we have prepared carbene complexes of the general formula *cis*-(or *trans*-)-$(RNC)(QC{=}NHR)PdX_2$ where (I) R = t-Bu; X = Cl, Br; Q = Me_2N, Et_2N, p-$CH_3 \cdot C_6H_4NH$, OMe; (II) R = t-Bu; X = I; Q = Me_2N, Et_2N; and (III) R = p-$Cl \cdot C_6H_4$; X = I; Q = OMe, OEt, p-$CH_3 \cdot C_6H_4 \cdot NH$ from the parent isocyanide complex *cis*-(or *trans*-)$(RNC)_2PdX_2$, by reaction with the appropriate substrate, QH. Yields range from 30–60%, and all the complexes have been characterised satisfactorily by elemental analysis, IR and NMR data.

Some striking trends are observed for the above reactions. Firstly, carbene formation becomes less facile as the electronegativity of the metal-coordinated halogen decreases so that, for example, methanol reacts with $(t\text{-}BuNC)_2PdCl_2$ at 25° but no reaction is observed with the corresponding diiodide even after 15 h at 100° A similar trend is observed with secondary alkyl amines (although here the diiodide does react after extended heating at 60°) suggesting that the primary effect is electronic rather than steric. This suggestion is reinforced by the observation that the triphenylphosphine substituted compound, $(t\text{-}BuNC)(PPh_3)PdCl_2$ is completely inert towards carbene formation. The ν(NC) stretching frequency is lowered by 12 cm^{-1} in this compound compared with the bis-isocyanide product, suggesting that the Ph_3P is functioning largely as a σ-donor. Secondly, as the ability of the R group in RNC to withdraw electrons becomes more effective a marked increase occurs in the reactivity of the coordinated isocyanide group. Thus while no carbene was observed with $(t\text{-}BuNC)_2PdI_2$ and p-toluidine, the corresponding $(p\text{-}Cl \cdot C_6H_4 \cdot NC)_2PdI_2$ reacts rapidly in refluxing chloroform.

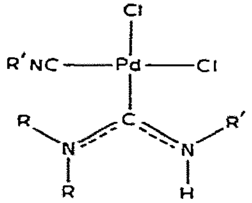
TABLE 1

INFRARED[a] AND NMR[b] DATA FOR DIMETHYLAMINOCARBENE COMPLEXES

Complex	*Coordinated RNC* τ*(t-Bu)*	*Carbene NMe*$_2$ τ*(Me)*	$\nu(N{\equiv}C)$ (cm^{-1})	$\nu(N\overset{-}{\cdots}C)$ (cm^{-1})	$\nu(N{-}H)$ (cm^{-1})	$\Delta\nu(N{\equiv}C)$[c] (cm^{-1})
$(t\text{-}BuNC)_2PdCl_2$	8.40		2250, 2264			127
$(t\text{-}BuNC)_2PdBr_2$	8.48		2233			106
$(t\text{-}BuNC)_2PdI_2$	8.48		2226			99
 $(t\text{-}BuNC)PdCl_2\left(C\begin{matrix}\diagup NH\text{-}t\text{-}Bu\\ \diagdown NMe_2\end{matrix}\right)$	8.25, 850	6.15, 6.83	2230	1565	3310	103
 $(t\text{-}BuNC)PdBr_2\left(C\begin{matrix}\diagup NH\text{-}t\text{-}Bu\\ \diagdown NMe_2\end{matrix}\right)$	8.28, 850	6.18, 6.85	2225	1565	3310	98
 $(t\text{-}BuNC)PdI_2\left(C\begin{matrix}\diagup NH\text{-}t\text{-}Bu\\ \diagdown NMe_2\end{matrix}\right)$	8.30, 8.47	6.26, 7.03	2210	1555	3350	83

[a] Measured as KBr discs. [b] Measured at 60 Mc/s in $CDCl_3$ soln. (at 35°). [c] Difference between complexed and free RNC.

The ^{1}H NMR spectra of the carbene complexes are interesting in view of the previous discussions for cationic carbene complexes of Pt^{II} [5,6,8]. For these latter complexes it appears that there may be either free or restricted rotation about the platinum—carbene bond depending upon the other ligands attached to the metal atom. In addition to this possibility the present compounds exhibit restricted rotation about the C$\overset{\cdot\cdot\cdot}{=}NR_2$ bond since in both the *cis*-(chloro-) and *trans*-(bromo- and iodo-) carbenes two distinct alkyl resonances from the NR$_2$ group are observed which coalesce to a singlet at higher temperatures. Our results at the moment are unable to provide any evidence concerning rotational freedom about the palladium—carbene bond. The spectral data for the dimethylaminocarbenes are given in Table 1.



The general variations in reactivity discussed above may be rationalised in terms of the coordinated isocyanide functioning primarily as a σ-donor, charge thus being removed from the carbon atom. The observed increase in the NC bond order on coordination to Pd^{II} implies that the electrons donated possess some antibonding character with respect to the NC bond, although undoubtedly the important factor is the overall charge distribution within the N—C→M system which facilitates attack, primarily at the carbon atom, by the incoming nucleophile. Using this scheme, the presence of electron withdrawing groups on both the metal and isocyanide ligand would be expected to maximise the reactivity of the NC group as is observed experimentally. While *cis* addition of the QH species is established for related Pt^{II} complexes[5] preliminary X-ray data on the (t-BuNC)$_2$PdI$_2$ shows the R—N—C bond to be essentially linear (angle of approx. 175°)[9] suggesting that initial electrophilic attack at the N atom is unlikely in this case.

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