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THE REACTION OF *endo*-METHOXYTETRAPHENYLCYCLOBUTENYLPALLADIUM HEXAFLUOROACETYLACETONATE WITH ORGANIC ISOCYANATES

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Summary

The complex [(*endo*)-C_4Ph_4OMe)Pdhfac] readily reacts with alkyl and aryl isocyanates in aprotic solvents, giving 1 : 1 insertion products which have been assigned *N*-bonded amidate structures of the type [(PhOMeC=CPhCPh=CPhC(O)NR)Pdhfac]. The rate of RNCO insertion is first order both in starting palladium complex and isocyanate substrate. A Hammett-type plot of log(rate constant) vs σ_p for the reaction of *para*-substituted aryl isocyanates is linear with a value of ρ = +1.13. A four-centred transition state is proposed which is consistent with the observation that electron-withdrawing groups on the isocyanate increase the rate of reaction.

Introduction

The "insertion" of organic isocyanates into transition metal—oxygen and —nitrogen bonds has been well documented [1—3]. However, there are few examples of the reaction of an isocyanate with a metal—carbon bond. In a brief communication, Vol'pin and coworkers reported the formation of the titanium metallocycle 1 from the interaction of [(η^5-C_5H_5)$_2$TiPh$_2$] with phenyl isocyanate [4]. Wilkins has also found that methyl complexes of Nb^V and Ta^V are

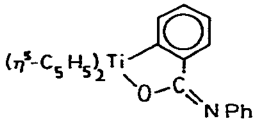

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TABLE 1

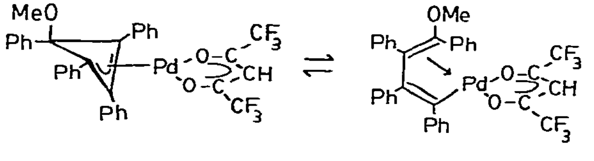
SELECTED ^{1}H NMR, INFRARED AND MASS SPECTROSCOPIC DATA FOR ISOCYANATE INSERTION PRODUCTS 3a—3h OBTAINED FROM THE REACTION OF 2 WITH RNCO

Product	RNCO	^{1}H NMR ($CDCl_3$, 34°C, δ ppm) (multiplicity)			Infrared data (cm^{-1})		Mass spectral data, major fragments, ion (assignment, m/e) ^{a}
		OCH_3	H(hfac)	R	ν(CO)	ν(CN)	
3a	Me	3.44(s)	6.13(s)	CH_3, 2.70(s)	1666	1153	$P^+ = [(C_2H_3NO)(C_4Ph_4OCH_3)Pdhfac]^+$ (757) $[(C_2H_3NO)(C_4Ph_4OCH_3)^+$ (444)
3b	Et	3.53(s)	6.22(s)	CH_3, 1.17(t, 7 hz); CH_2, 3.21(q, 8 hz)	1663	1150	$P^+ = [(C_3H_5NO)(C_4Ph_4OCH_3)Pdhfac]^+$ (771) $[(C_3H_5NO)(C_4Ph_4OCH_3)]^+$ (458)
3c	n-Pr	3.57(s)	6.23(s)	CH_3, 0.70(t, 7 hz); $MeCH_2$, 1.67(m); $MeCH_2CH_2$, 3.07(t, 8 hz)	1665	1150	$P^+ = [(C_4H_7NO)(C_4Ph_4OCH_3)Pdhfac]^+$ (785) $[(C_4H_7NO)(C_4Ph_4OCH_3)]^+$ (472)
3d	t-Bu	3.68(s)	6.25(s)	$(CH_3)_3C$, 1.45(s)	1645	1148	$P^+ = [(C_5H_9NO)(C_4Ph_4OCH_3)Pdhfac]^+$ (799) $[(C_5H_9NO)(C_4Ph_4OCH_3)]^+$ (486)
3e	C_6H_5	3.84(s)	6.27(s)	Ph, 6—7(m)	1660	1150	$P(\text{org.})^+ = [(C_7H_5NO)(C_4Ph_4OCH_3)]^+$ (506)
3f	p-MeC_6H_4	3.86(s)	6.30(s)	CH_3, 2.11(s); C_6H_4, 6—7(m)	1670	1145	$P(\text{org.})^+ = [(C_8H_7NO)(C_4Ph_4OCH_3)]^+$ (520)
3g	p-FC_6H_4	3.88(s)	6.36(s)	C_6H_4, 6—7(m)	1670	1147	$P(\text{org.})^+ = [(C_6H_4NOF)(C_4Ph_4OCH_3)]^+$ (524)
3h	p-ClC_6H_4	3.80(s)	6.26(s)	C_6H_4, 6—7(m)	1665	1148	

^{a} Based on ^{106}Pd.

reactive towards methyl and phenyl isocyanate, and acetamido complexes of the type $[MeMCl_2(RNC(O)Me)_2]$ and $[MCl_n(RNC(O)Me)_{5-n}]$ (R = Me, Ph; n = 2, 3) have been isolated from the reaction mixtures [5]. On the basis of the rather low values of ν(CO) for these compounds, it was proposed that bonding to the metal atom through both oxygen and nitrogen was occurring [5]. In addition, several reports of transition metal-mediated reactions of organic substrates with isocyanates have appeared which probably involve the "insertion" of RNCO into a metal—carbon bond [6—8].

We have shown that the complex [(*endo*)-C_4Ph_4OMe)Pdhfac], 2, which exists in solution as an equilibrium mixture of η^3-cyclobutenyl and η^1-butadienyl forms (i.e., 2a $\rightleftharpoons$ 2b) [9], is highly reactive towards olefins, 1,2-dienes and 1,3-dienes [10]. We now report that 2 readily reacts with both alkyl and aryl isocyanates in aprotic solvents.

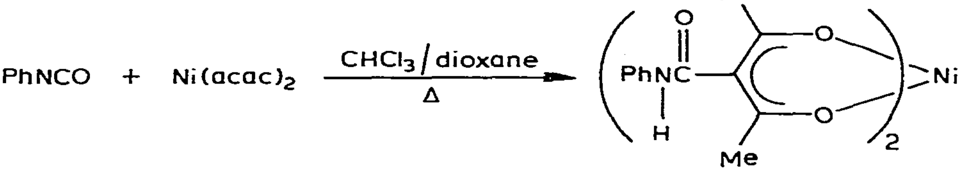


2a 2b

Results and discussion

One equivalent of the isocyanate was added to a $CDCl_3$ solution of 2, and the reaction monitored by ^1H NMR. The methoxy resonances associated with 2a $\rightleftharpoons$ 2b disappeared at about the same rate as a single new OMe peak of the product grew in at higher field. The insertion products 3a—3h were obtained by evaporation of the solvent and chromatographic workup as yellow-brown glasses. Characterisation was performed by ^1H NMR, infrared and mass spectrometry and elemental analysis. These are all consistent with the insertion of a single molecule of RNCO per palladium atom.

Mass spectra of the products (Table 1) contained peaks corresponding to the organic fragment $[(RNCO)C_4Ph_4OMe)]^+$ and $[Hhfac]^+$ (208 m/e^+) in all cases. In addition, the products obtained from the alkyl isocyanate reactions, 3a—3d, showed a parent molecular ion peak. There was no evidence for the insertion of a second molecule of isocyanate ($[(RNCO)_2(C_4Ph_4OMe)]^+$ not observed) and no peak associated with the species $[(RNCO)(hfac)]^+$ was detected. This latter fact is significant in light of recent reports by Nelson et al. of the insertion of isocyanates into the C—H bond of β-diketonate and β-ketoimine compounds of Cu^{II} and Ni^{II} [11,12].

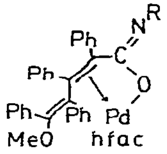


Infrared spectra of the isocyanate insertion products 3a—3h showed, in addition to absorptions characteristic of the hfac ligand, (ν(CO) 1630—1635 cm^{-1}), two new bands in the regions 1645—1670 cm^{-1} and 1145—1153 cm^{-1} (Table 1). No peaks corresponding to ν(NH) were observed at higher frequencies (3300—3400 cm^{-1}), again sugggesting that insertion of RNCO into the hfac C—H bond had not occurred.

^{1}H NMR spectra of the compounds 3a—3h are consistent with a single solution species (Table 1). Thus, for example, the ^{1}H NMR spectrum of 3a, obtained from the reaction of 2 with MeNCO showed a single methoxy peak at δ 3.44 ppm (s, 3p), a singlet at δ 2.70 ppm (s, 3p) for the methyl group from the isocyanate, while the C—H proton of the hfac group came at δ 6.13 ppm (s, 1p).

A ^{19}F NMR of the *p*-fluorophenyl isocyanate insertion product 3g showed a multiplet at δ 102.77 ppm (t of t, ^3J(H—F) = 8.5 Hz, ^4J(H—F) = 5 Hz) for the fluorine atom on the phenyl ring, and a singlet at δ 69.88 ppm associated with the CF_3 groups of the hfac moiety. At low temperatures this hfac signal was split into two singlets of equal intensity, indicating that an exchange of the β-diketonate oxygens in an unsymmetric complex is taking place. Exchange of this type has been observed in acac and hfac complexes of Pd^{II} when two strong *trans* directing groups are present in the molecule [13]. However, in the case of complex 3g, the rate of CF_3 site exchange was found to be concentration dependent and hence an intermolecular process must be occurring.

Several possible structures may be considered for the isocyanate insertion products 3a—3h. A complex similar to 1 in which an uncoordinated -C=N group is present, i.e., 4 or 5, may be eliminated on the basis of the infrared data since the observed band at 1645—1670 cm^{-1} is too high in frequency for ν(C=N) [4]. Similarly, ν(CO) for a *N*,*O*-bonded bidentate amidate compound of type 6 would be expected at about 1600 cm^{-1} [5]. However, the 1645—1670 cm^{-1} peak associated with 3a—3h is consistent with a substituted amide function [14] and the lower frequency band (1145—1153 cm^{-1}) may then be



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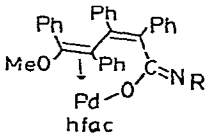

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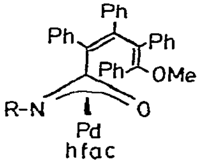

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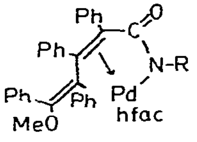
assigned to ν(CN). Two isomers incorporating this type of bonding are possible, 7 and 8, in which complexation to either C=C double bond of the butadiene



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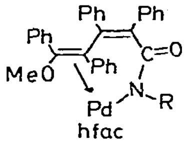

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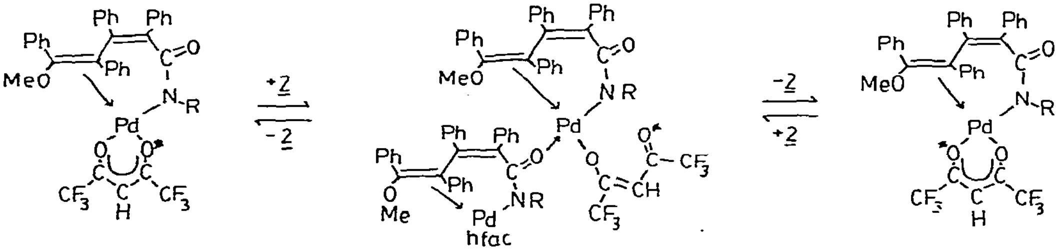
moiety completes the coordination about the metal. While spectroscopic evidence cannot distinguish between these two structures, 8 is favoured on the basis of molecular models and since it involves the formation of the preferred six-membered chelate ring.

The presence of a free ketonic function in the insertion products may then be used to explain the observed intermolecular exchange of CF_3 groups on the hfac moiety. As shown in Scheme 1, the -C=O group of one complex can serve

SCHEME 1

MECHANISM OF INTERMOLECULAR CF_3 SITE EXCHANGE IN hfac LIGAND OF INSERTION PRODUCTS 3a—3h.



as a donor ligand towards another palladium, thereby creating a monodentate hfac group which may rechelate to the metal, thus scrambling CF_3 groups. It is noteworthy that a similar type of intermolecular exchange process has been proposed to account for the *syn,syn* and *anti,anti* interchange of allylic protons in the complex [(η^3-allyl)Pd(α-picolinate)] [15].

The rate of the reaction of RNCO with 2, as monitored by ^{1}H NMR spectroscopy, was found to vary considerably depending upon the nature of the R group on the isocyanate. Second order rate plots (first order each in [2] and [RNCO]) gave good linear fits in all cases (Fig. 1). A relative order of reactivity of the isocyanate of R = p-ClC$_6$H$_4$ (230) > p-FC$_6$H$_4$ (147) > C$_6$H$_5$ (133) > p-MeC$_6$H$_4$ (84) >> Et (3.3) > n-Pr (1.9) > Me (1.1) >> t-Bu (0.4) was established (second order rate constant, k, in brackets in l mole^{-1} min^{-1} $\times 10^3$ at 34°C). Furthermore, a plot of log k vs σ_p for the p-XC$_6$H$_4$NCO reactions was linear (Fig. 2), and gave a value for the reaction constant ρ of +1.13.

While the variation in the *para* substituents is somewhat limited, the positive value of ρ is consistent with a reaction centre which is facilitated by the reduction of electron density [16,17]. If the charge separations associated with a plausible four-centered intermediate in the reaction of the isocyanate with

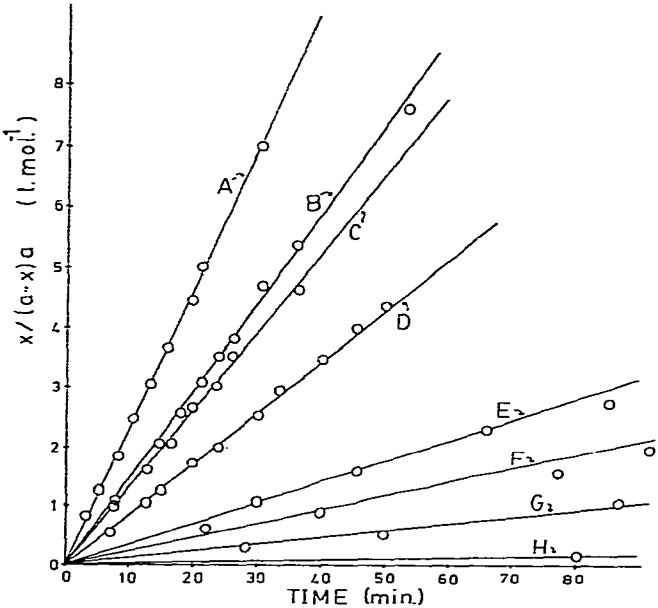


Fig. 1. Second order rate plots for reaction of RNCO with [(*endo*-C_4Ph_4OMe)Pdhfac]. Initial concentrations of 2 = initial concentration of RNCO = 0.494 *M* in $CDCl_3$ at 34°C. Plot A, *p*-ClC_6H_4NCO; B, *p*-FC_6H_4NCO; C, C_6H_5NCO; D, *p*-MeC_6H_4NCO; E, EtNCO; F, n-PrNCO; G, MeNCO; H, t-BuNCO. [a = initial concentration of 2; x = concentration of insertion product at time (t)].

[(*endo*-C_4Ph_4OMe)Pdhfac] are considered (Fig. 3), it is apparent that electron-withdrawing substituents on the R group of the isocyanate will reduce the negative charge associated with the isocyanate nitrogen, thereby facilitating reaction. This is consistent with the positive ρ value, and with the fact that alkyl isocyanate insertion is slower than aryl isocyanate reaction (alkyls are

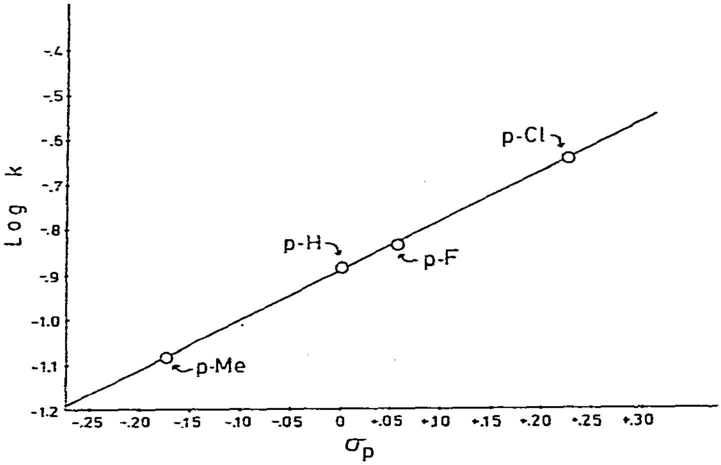


Fig. 2. Plot of log(second order rate constant) vs σ_p for reaction of 2 with *p*-XC_6H_4NCO (X = Cl, F, H, Me).

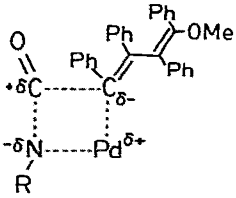


Fig. 3. Four-centred transition state formed in reaction of [(*endo*-C_4Ph_4OMe)Pdhfac] with RNCO, showing charge separations (δ) involved.

relatively electron donating compared to aryl groups). In the alkyl isocyanate reactions steric factors as well as electronic ones affect the rate as evidenced by the large decrease in k on going from R = n-Pr to R = t-Bu. However, the relative rate of MeNCO insertion is anomalously low and cannot be explained on the basis of either steric or electronic factors or a combination of both [16,17].

A four-centred intermediate similar to that of Fig. 3 has been proposed by several workers for the reaction of aryl isocyanates with alcohols to produce urethanes [18,19]. Significantly, these reactions also show linear plots for log k vs σ_p and have positive ρ values [20,21].

The reaction of RNCO with 2 probably proceeds by coordination of the isocyanate to the ring-opened butadienyl form 2b through the π system of the C=N bond [23]. Insertion of the isocyanate into the palladium—dienyl bond may then occur via the four-centred intermediate of Fig. 3 to give the *N*-bonded amidate products 7 or 8. In contrast to the facile reaction of isocyanates with 2, we have observed no reaction of RNCO compounds with [(η^3-allyl)Pdhfac] even after several months. Furthermore, ^{1}H NMR spectra of the reaction mixtures give no indication of the presence of a dynamic σ-allyl species. Since a σ-allylic species has been shown to be the reactive intermediate in the insertion of unsaturated hydrocarbons into π-allylPd complexes [23], it is probable that the RNCO molecule is too weak a π donor to promote the σ-allyl formation, hence further reaction does not occur.

Experimental

Experimental details for the preparation of the starting palladium complex have been described previously [10]. Organic isocyanates were commercial samples, used as obtained, except for phenyl isocyanate which was freshly distilled prior to reaction. The preparation of the insertion products 3a—3h were all quite similar with yields ranging from 80—90%. Satisfactory elemental analyses were obtained in all cases. A typical preparative example is given.

Complex 3a; insertion product of [(endo-C_4Ph_4OMe)Pdhfac] and methyl isocyanate

0.145 g of the palladium complex 2 was dissolved in 5 ml CH_2Cl_2 and 23 μl of methyl isocyanate was syringed in. The solution was left stirring overnight. Evaporation of the solvent and chromatography of the residue through a short florisil column (eluting with cyclohexane) gave a bright yellow solution from which was obtained 3a as a yellow glass, on pumping. Yield, 0.13 g (80%), m.p.

85–88°C. Analysis; Found: C, 56.82; H, 3.69. Calcd for $C_{31}H_{27}NO_4F_6Pd$: C, 57.04; H, 3.59%.

Kinetic studies

These were performed at 34°C with the use of ^{1}H NMR spectroscopy, measuring the relative concentrations of reactants and products by integration of the respective methoxy resonances at convenient time intervals. 400 μl of 0.494 *M* solutions of [(*endo*-C_4Ph_4OMe)Pdhfac] in $CDCl_3$ were employed, to which 1 equivalent of the isocyanate was added, either by syringe or in the case of *p*-chlorophenyl isocyanate, as a solid.

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