Phenylation of Cationic Allyl Palladium(II) Complexes by Tetraphenylborate. Synthesis of α-Diimine Olefin Palladium(0) Complexes and Mechanistic Aspects

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The cationic allyl complexes $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{–}N')]^+$ (N–N′ = α-diimine ligand; R^1 = H or Me) react with BPh_4^- in the presence of activated olefins to give $[Pd(\eta^2\text{-olefin})(N\text{–}N')]$ (olefin = fumaronitrile, dimethyl fumarate or maleic anhydride) and $PhCH_2C(R^1){=}CH_2$. The palladium(0) derivatives can be isolated in good yield and have been characterized by elemental analysis, molecular weight measurements and standard spectroscopic techniques. The reaction rates increase with increasing π-accepting ability of the α-diimine, with decreasing steric requirements of the imino carbon substituents and with decreasing stability towards palladium–nitrogen bond breaking in the parent cationic compounds. The rates also increase with decreasing relative permittivity and co-ordinating properties of the solvent. Kinetic measurements in aqueous (2% v/v) methanol provide pseudo-first-order rate constants that are independent of both BPh_4^- and olefin concentrations. This has been interpreted on the basis of extensive ion pairing between the cationic substrate and the BPh_4^- anion, followed by rate-determining phenyl transfer to the palladium centre and fast reductive elimination of allylbenzenes.

Many palladium(0) complexes with η^2-bonded olefins of the type $[Pd(olefin)L_2]$ are reported in the literature with L_2 = tertiary phosphines, isocyanides or α-diimines.[1] In particular, the preparation of α-diimino complexes involves displacement of benzylideneacetone ligands from pre-formed palladium(0) derivatives by 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen),[2] or 1,2-bis(imino)ethanes.[3] In the course of a study on the solution behaviour of the pyridine-2-carbaldimine complexes $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(C_5H_4N\text{-}2\text{-}CH{=}NR^2)]X$, we noted that the complex with $R^2 = C_6H_4OMe\text{-}4$ and $X = BPh_4^-$ underwent rapid decomposition to give $PhCH_2C(Me){=}CH_2$ and palladium metal at ambient temperature.[4] If the reaction is carried out in the presence of activated olefins, the palladium(0) compounds $[Pd(olefin)(C_5H_4N\text{-}2\text{-}CH{=}NR^2)]$ are readily obtained. We report herein the details of such a synthetic method, which can be extended to a variety of α-diimino ligands. A kinetic investigation of the reaction mechanism has also been carried out, and the results are discussed in comparison with a recently published arylation mechanism of cationic platinum(II) complexes with BR_4^- anions (R = aryl).[5]

Results and Discussion

Preparation and Characterization of [Pd(olefin)(N–N′)] *Complexes.*—The mixed α-diimine–olefin palladium(0) complexes given in Table 1 are prepared by the general reaction (1)

$$[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{–}N')]^+ + BPh_4^- \xrightarrow[-BPh_3]{+\text{olefin}} [Pd(\text{olefin})(N\text{–}N')] + PhCH_2C(R^1){=}CH_2 \quad (1)$$

[N–N′ = $R^2N{=}CH\text{–}CH{=}NR^2$ ($R^2 = C_6H_4OMe\text{-}4$ or CMe_3), $R^2N{=}C(Me)\text{–}C(Me){=}NR^2$ ($R^2 = C_6H_4OMe\text{-}4$), $C_5H_4N\text{-}2\text{-}CH{=}NR^2$ ($R^2 = C_6H_4OMe\text{-}4$, Me or CMe_3), bipy or phen; R^1 = H or Me; olefin = fumaronitrile (fn), dimethyl fumarate (dmf) or maleic anhydride (ma)].

Three different methods of preparation can be employed as detailed in Table 1. Method (*a*) involves the reaction of substrates $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{–}N')]ClO_4$ with $NaBPh_4$ (1:1 molar ratio), in the presence of a slight excess of the olefin, in acetone at 25 °C. In method (*b*) the pre-formed complexes $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{–}N')]BPh_4$ are dissolved in CH_2Cl_2, containing the required olefin in a 1:1.2 molar ratio, at 30 °C. Method (*c*) consists in treating the allyl chloro-bridged dimers $[\{PdCl(\eta^3\text{-}2\text{-}R^1C_3H_4)\}_2]$ with the α-diimine ($C_5H_4N\text{-}2\text{-}CH{=}NR^2$ or bipy), $NaBPh_4$ and the olefin (0.5:1:1:1.2 molar ratio) in 1,2-dichloroethane at 50 °C. Method (*a*) is employed for the cationic complexes $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{–}N')]^+$ (N–N′ = $R^2N{=}CH\text{–}CH{=}NR^2$), whose high reactivity towards the BPh_4^- anion (even in the solid state) prevents their isolation as BPh_4^- salts (see Experimental section). Method (*b*) is largely preferred and gives better yields whenever the $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{–}N')]BPh_4$ substrates are accessible. Method (*c*), while not requiring prior preparation of $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{–}N')]^+$ cations, gives lower yields owing to partial decomposition of the products to palladium metal as a result of the higher reaction temperature used. The progress of reaction can be monitored by following changes in electrical conductivity and in electronic spectra (500–300 nm) of properly diluted reaction mixtures [methods (*a*) and (*b*)], changes in the solution IR spectra relative to ν(C=O) and ν(C≡N) of the reacting olefin in the ranges 1800–1600 and 2300–2150 cm^{-1}, respectively [methods (*b*) and (*c*)], and by changes in the ^1H NMR spectra in CD_2Cl_2 [method (*b*)].

Reaction (1) involves transfer of a phenyl group from BPh_4^- to the η^3-bound allyl moiety, resulting in the formation of allylbenzenes, BPh_3 and an α-diimine palladium(0) fragment, which is stabilized by η^2-co-ordination of the activated olefin. The allylbenzenes are formed in almost quantitative yield

Table 1 Preparation, elemental analyses, molecular weights and selected IR data for [Pd(olefin)(N–N′)]

			Preparation				Analysis (%)[d]			IR	IR bands[e]/cm^{-1}		
Compound	Olefin	R^2	Method[a]	R^1[b]	Reaction time/h	Yield[c] (%)	C	H	N	*M*	ν(C≡N)[f]	ν(C=O)[f]	ν(C=N)[g]
[Pd(olefin)(R^2N=CH–CH=NR^2)]	fn	C_6H_4OMe-4	(*a*)	Me	1	79.5	52.8 (53.05)	3.9 (4.00)	12.2 (12.40)	*h*	2197s		1578vs
	dmf	C_6H_4OMe-4	(*a*)	Me	1	73.2	50.7 (50.95)	4.6 (4.65)	5.4 (5.40)	*h*		1690s, 1678vs	1581s, 1572s
	fn	CMe_3	(*a*)	H	2	74.3	47.5 (47.65)	6.3 (6.30)	15.8 (15.90)	*i*	2196s		1588w
[Pd(olefin){R^2N=C(Me)–C(Me)=NR^2}]	fn	C_6H_4OMe-4	(*b*)	Me	1.5	83.2	54.7 (54.95)	4.5 (4.60)	11.7 (11.65)	505 (480.8)	2197s		1578ms
[Pd(olefin)(C_5H_4N-2-CH=NR^2)]	fn	C_6H_4OMe-4	(*b*)	Me	2.5	75.7	51.2 (51.45)	3.5 (3.55)	14.0 (14.10)	*h*	2197s		1615m
			(*b*)	H	2	70.6							
	dmf	C_6H_4OMe-4	(*b*)	Me	2.5	80.9	49.3 (49.30)	4.3 (4.35)	6.1 (6.05)	455 (462.8)		1685(sh), 1670s	1616m
			(*c*)	Me	4	73.5							
			(*a*)	H	12	57.0							
			(*b*)	H	2	74.0							
			(*c*)	H	2	60.5							
	fn	Me	(*b*)	H	3.5	78.8	43.1 (43.35)	3.2 (3.30)	18.2 (18.40)	330 (304.6)	2197s		1637mw
	fn	CMe_3	(*b*)	H	4	75.0	48.3 (48.50)	4.5 (4.65)	16.1 (16.15)	342 (346.7)	2197s		1627mw
			(*c*)	H	4	60.6							
	dmf	CMe_3	(*b*)	H	5	72.7	46.4 (46.55)	5.4 (5.35)	6.7 (6.80)	407 (412.8)		1680vs	1627mw
	ma	CMe_3	(*b*)	H	6	76.4	45.7 (45.85)	4.4 (4.40)	7.6 (7.65)	377 (366.7)		1786s, 1761m, 1720s	1626mw
			(*c*)	H	5	71.0							
[Pd(fn)(bipy)]			(*b*)	H	5	76.3	49.0 (49.35)	2.9 (2.95)	16.2 (16.45)	*h*	2195s		
[Pd(dmf)(bipy)]			(*c*)	H	7	60.0	47.0 (47.25)	3.9 (3.95)	6.8 (6.90)	420 (406.7)		1691s, 1679vs	
[Pd(fn)(phen)]			(*b*)[j]	H	72	82.3	52.2 (52.70)	2.6 (2.75)	15.1 (15.35)	*h*	2195s		

[a] See Experimental section for preparation details. [b] Allyl substituent in the parent compound [Pd(η^3-2-$R^1C_3H_4$)(N–N′)]$^+$. [c] Based on the theoretical amount. [d] Calculated values in parentheses. [e] As Nujol mulls. [f] Vibrations of co-ordinated olefin. [g] Vibration of α-diimine ligand. [h] Scarcely soluble in 1,2-dichloroethane. [i] Fast decomposition to palladium metal. [j] At 40 °C.

Table 2 Hydrogen-1 NMR data (δ) for [Pd(olefin)(N–N′)] complexes in CD_2Cl_2[a]

			Imino protons	2-Pyridyl protons[b]					Olefinic protons	
Compound	Olefin	R^2	N=CH	H^3	H^4	H^5	H^6	N–R protons	=CH	O–CH_3
[Pd(olefin)(R^2N=CH–CH=NR^2)]	fn	C_6H_4OMe-4[c]	8.48(s)					3.86(s)[d]	3.0(s,br)	
	fn	CMe_3	8.11(s)					1.45(s)[e]	2.79(s)	
[Pd(olefin){R^2N=C(Me)–C(Me)=NR^2}]	fn	C_6H_4OMe-4	2.27(s)[f]					3.83(s)[d]	2.60(s)	
[Pd(olefin)(C_5H_4N-2-CH=NR^2)]	fn	C_6H_4OMe-4[c]	8.67(s)	7.80(m)	8.05(m)	7.58(m)	8.83(m)	3.86(s)[d]	2.96(s)	
	dmf	C_6H_4OMe-4	8.67(s)	7.76(m)	7.93(m)	7.42(m)	8.63(m)	3.83(s)[d]	3.80(sh)	3.56(s)
	fn	Me	8.38(q) ^4J(HMe) 1.6	7.67(m)	8.02(m)	7.58(m)	8.85(m)	3.90(d)[g]	2.87(s)	
	fn	CMe_3	8.37(s)	7.69(m)	8.02(m)	7.57(m)	8.85(m)	1.51(s)[e]	2.87(s)	
	dmf	CMe_3	8.32(s)	7.62(m)	7.95(m)	7.50(m)	8.75(m)	1.41(s)[e]	3.70[h]	3.56(s), 3.53(s)
	ma	CMe_3	8.33(s)	7.67(m)	8.00(m)	7.54(m)	8.75(m)	1.44(s)[e]	3.89(s)	
[Pd(fn)(bipy)][c]				8.17(m)	8.04(m)	7.55(m)	8.95(m)		2.93(s)	
[Pd(dmf)(bipy)]				8.11(m)	7.95(m)	7.42(m)	8.72(m)		3.85(s)	3.60(s)
				1,10-Phenanthroline protons						
				H^5,H^6	H^4,H^7	H^3,H^8	H^2,H^9			
[Pd(fn)(phen)][c]				7.97(s)	8.51(dd) ^3J(HH) 8.3 ^4J(HH) 1.5	7.85(dd) ^3J(HH) 4.8	9.25(dd)		3.06(s)	

[a] $SiMe_4$ as internal standard, at 30 °C; s = singlet, d = doublet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad, sh = shoulder; coupling constants in Hz; satisfactory integration values are obtained. [b] The 2-pyridyl protons give rise to second-order spectra, in which each proton appears as a multiplet of characteristic pattern. [c] Saturated solution. [d] Methyl protons of the NC_6H_4OMe-4 group. [e] N–CMe_3 protons. [f] N=CMe protons. [g] N–Me protons. [h] Centre of an AB spin system with ^3J(HH) = 9.0 Hz.

(>95%), as indicated by ^{1}H NMR spectra and GC–MS experiments {as an example, for $PhCH_2CH=CH_2$, δ_H 6.20–5.70 (1 H, m, CH), 5.20–4.90 (2 H, m, $CH=CH_2$) and 3.35 [2 H, d, ^3J(HH) 6.6 Hz, $PhCH_2$]; M^+ 118}.

The BPh_3 product cannot be isolated as such because it subsequently reacts with atmospheric oxygen and/or trace amounts of water in the system.[6] In fact, the attempted isolation of BPh_3 as its 4-(dimethylamino)pyridine (4-dmapy) adduct from the reaction of $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(C_5H_4N\text{-}2\text{-}CH=NC_6H_4OMe\text{-}4)]BPh_4$ with dmf in CH_2Cl_2, under nitrogen, led instead to $Ph_2(OH)B$(4-dmapy) (see Experimental section). The latter product clearly originates from hydrolysis of the B–Ph bond, which also accounts for the detection of a small amount of benzene (which increases with time) during ^{1}H NMR monitoring of the above reaction in CD_2Cl_2. The primary BPh_3 product also gives an adduct with the palladium(0)-η^2-bound fumaronitrile, as shown by the IR spectra of the reaction mixtures in CH_2Cl_2, containing fumaronitrile as the olefin, which exhibit two ν(C≡N) bands at around 2200 and 2280 cm^{-1}. The former is due to the complex [Pd(fn)(N–N′)], whereas the latter is attributed to an equilibrium adduct between BPh_3 and the cyano group of the η^2-bound fumaronitrile through 'head-on' nitrogen–boron linkage. The establishment of such an equilibrium is confirmed by IR spectral changes in the range 2300–2150 cm^{-1} brought about by addition of increasing amounts of BPh_3 (up to a 1:1 molar ratio) to a CH_2Cl_2 solution of $[Pd(fn)(C_5H_4N\text{-}2\text{-}CH=NMe)]$, whereby the ν(C≡N) band at 2205 cm^{-1} decreases with concomitant increase of the ν(C≡N) absorption of the BPh_3 adduct at 2280 cm^{-1}.

Reaction (1) requires an anion:cation molar ratio of at least 1:1 to go to completion. For lower ratios, the reaction proceeds only partially. In fact, the ^{1}H NMR spectra of the systems $NaBPh_4$–$[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(4\text{-}MeOC_6H_4N=CH\text{-}CH=NC_6H_4OMe\text{-}4)]ClO_4$–fn (0.5:1:1.2) in $(CD_3)_2CO$ and NBu_4BPh_4–$[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(C_5H_4N\text{-}2\text{-}CH=NC_6H_4OMe\text{-}4)]ClO_4$–fn (0.5:1:1.2) in CD_2Cl_2 show that the reaction occurs only to an extent of *ca.* 50%. These results suggest that the actual phenylating agent is the BPh_4^- anion, without any appreciable contribution by the BPh_3 species produced in the reaction. Consistently, no phenyl transfer is observed on treating the complex $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(C_5H_4N\text{-}2\text{-}CH=NC_6H_4OMe\text{-}4)]ClO_4$ with BPh_3 (B:Pd 1.2:1) in the presence of fumaronitrile, in either CH_2Cl_2 or CH_2Cl_2–MeOH (1:1 v/v) at 30 °C. By contrast, all three phenyl groups of BPh_3 were transferred to platinum in the reaction with the solvento derivatives *cis*-$[Pt(solv)_2L_2]^{2+}$ (solv = H_2O or MeOH, L = tertiary phosphine) to yield *trans*-$[PtPh(solv)L_2]^+$.[5]

Changes of specific conductivities with time indicate that the rates of reaction (1) depend on: (*i*) the α-diimine ligand N–N′, (*ii*) the allyl substituent R^1, (*iii*) the solvent used and (*iv*) the presence of co-ordinating species.

(*i*) In acetone [method (*a*)], the following reactivity trend is observed: $4\text{-}MeOC_6H_4N=CH\text{-}CH=NC_6H_4OMe\text{-}4 > Me_3C\text{-}N=CH\text{-}CH=NCMe_3 > 4\text{-}MeOC_6H_4N=C(Me)\text{-}C(Me)=NC_6H_4OMe\text{-}4$. In CH_2Cl_2 [method (*b*)], the reactivity orders are: $C_5H_4N\text{-}2\text{-}CH=NC_6H_4OMe\text{-}4 > C_5H_4N\text{-}2\text{-}CH=NMe \approx C_5H_4N\text{-}2\text{-}CH=NCMe_3$; and bipy ≫ phen. In general, the different types of α-diimino ligands display the following order for the same *N*-substituent R^2: $R^2N=CH\text{-}CH=NR^2 > C_5H_4N\text{-}2\text{-}CH=NR^2 >$ bipy ≫ phen ($R^2 = C_6H_4OMe$-4 or CMe_3).

These findings suggest that both the steric and electronic properties of the α-diimine are important: the rates of reaction increase with the increasing π-accepting ability of the N–N′ ligand[7] and with the decreasing steric requirements of the imino-carbon substituents. The comparable reactivity of $C_5H_4N\text{-}2\text{-}CH=NMe$ and $C_5H_4N\text{-}2\text{-}CH=NCMe_3$ substrates indicates that bulkiness of the imino-nitrogen substituent has little, if any, influence.

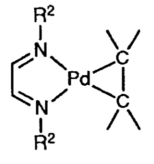
(*ii*) The reactivity decreases slightly on changing the R^1 allyl substituent from H to Me, suggesting that steric crowding at the C(2) allyl carbon is of some importance in the activation process.

(*iii*) A marked solvent effect is observed, with the rates of reaction decreasing in the order: $CH_2Cl_2 > CH_2ClCH_2Cl > Me_2CO >>> MeCN$ (*i.e.*, with increasing relative permittivity and co-ordinating ability of the solvent).

(*iv*) The rates of reaction in CH_2Cl_2 are depressed progressively upon the addition of increasing amounts of MeOH or of a co-ordinating ligand such as Cl^- ions or free α-diimine. On the other hand, the rates appear to be hardly affected by the nature of the activated olefin.

All the palladium(0) complexes in Table 1 are air-stable in the solid state, whereas in solution palladium metal is deposited slowly, with the rate of decomposition decreasing from 1,2-bis(imino)ethane to pyridine-2-carbaldimine derivatives. The [Pd(olefin)(N–N′)] complexes have been characterized by elemental analysis, IR spectra and molecular weight measurements (Table 1), and by ^{1}H NMR spectroscopy (Table 2).

The analytical and spectral data of $[Pd(dmf)(R^2N=CH\text{-}CH=NR^2)]$ ($R^2 = C_6H_4OMe$-4) and [Pd(dmf)(bipy)] are in good agreement with those reported for the same compounds prepared previously in a different way.[2,3] The structure and bonding in $[Pd(olefin)(R^2N=CH\text{-}CH=NR^2)]$ has already been described by Vrieze and co-workers.[3] In particular, they highlighted a predominant electron-density drift from the d^{10} metal centre to the activated olefin, in a planar arrangement, with a relevant contribution of the limiting structure **I**. The electronic structure of the olefin is highly modified on co-ordination, whereas that of the *N*,*N*′ chelating α-diimino ligand is hardly changed.



I

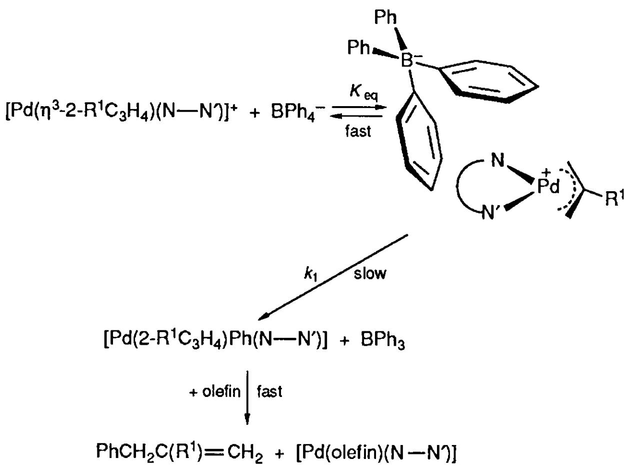
The new compounds in Tables 1 and 2 exhibit IR and ^{1}H NMR data fully in accord with this view. Thus, the spectral data for the α-diimine moieties are fairly close to those observed in the palladium(II) complexes $[PdCl_2(N\text{-}N')]$ and $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{-}N')]^+$, in which they behave as *N*,*N*′ chelating ligands.[4,8–10] The imino and 2-pyridyl proton resonances of [Pd(olefin)(N–N′)] appear to be only slightly shifted upfield (δ 0.1—0.4) relative to the corresponding signals of $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{-}N')]ClO_4$ in CD_2Cl_2 (see Table 4). A formal decrease in the palladium oxidation state from +2 to 0 does not cause any relevant change in the palladium-α-diimine bond, the increased electron density on the metal being substantially removed by extensive d→π* back bonding with the activated olefin, as is shown by the large upfield shifts of the olefinic proton resonances and the low-frequency shifts of the olefinic ν(C≡N) or ν(C=O) bands, compared to those of the free unco-ordinated ligands [*cf.* the olefinic δ_H values of 6.29 (fn), 6.81 (dmf) and 7.03 (ma) in CD_2Cl_2; the ν(C≡N) band at 2244 cm^{-1} (fn), and the ν(C=O) bands at 1725 cm^{-1} (dmf), and at 1850, 1792 and 1780 cm^{-1} (ma) in CH_2Cl_2]. The π-accepting ability of the olefin seems to play an important role in stabilizing the [Pd(olefin)(N–N′)] complexes: an attempt to prepare an analogous compound with N–N′ = $C_5H_4N\text{-}2\text{-}CH=NC_6H_4OMe$-4 and olefin = methyl vinyl ketone by method (*b*) failed owing to extensive decomposition to palladium metal.

In the ^{1}H NMR spectra of most of $[Pd(olefin)(C_5H_4N\text{-}2\text{-}CH=NR^2)]$ compounds at 30 °C, the olefinic protons are detected as a singlet despite the asymmetric structure of the α-diimino ligand. The time-averaged equivalence of these protons may result from (*i*) fast (on the NMR time-scale) dissociative processes involving either the palladium–olefin bond or one of the palladium–nitrogen bonds, or (*ii*) fast rotation of the olefin around the palladium–olefin bond axis. Some dissociation with release of free dmf is detected in the IR spectra of [Pd(dmf)-

Table 3 Pseudo-first-order rate constants for the reaction of [Pd(η^3-2-$R^1C_3H_4$)(N-N')]ClO_4 with an excess of $NaBPh_4$ and olefin at 25 °C in aqueous (2% v/v) methanol

N-N'	R^1	Olefin	$10^3k_{obs}/s^{-1}$
R^2N=CH-CH=NR^2			
$R^2 = C_6H_4OMe$-4	Me	dmf	*a*
CMe_3	Me	dmf	*a*
R^2N=C(Me)-C(Me)=NR^2			
$R^2 = C_6H_4OMe$-4	Me	dmf	0.5 (±0.1)
C_5H_4N-2-CH=NR^2			
$R^2 = CMe_3$	H	dmf	0.75 (±0.08)
CMe_3	H	fn	0.8 (±0.1)
Me	H	dmf	0.6 (±0.1)
C_6H_4OMe-4	H	dmf	2.98 (±0.07)
C_6H_4OMe-4	H	fn	2.9 (±0.1)
C_6H_4OMe-4	Me	dmf	1.8 (±0.2)
C_6H_4OMe-4	Me	fn	1.9 (±0.3)
bipy	H	dmf	0.17 (±0.05)
phen	H	fn	*b*

[a] Too fast to measure. [b] Too slow to measure.



Scheme 1 Proposed mechanism for reaction (1)

(R^2N=CH-CH=NR^2)] (R = C_6H_4OMe-4) in dilute 1,2-dichloroethane solution (*ca.* 5×10^{-3} mol dm^{-3}), whereas all the other dmf derivatives appear to be quite stable towards olefin dissociation under comparable conditions (*cf.* also molecular weight data in Table 1). However the peculiar behaviour of [Pd(dmf)(C_5H_4N-2-CH=$NCMe_3$)], whose olefinic protons appear as an AB spin system at 30 °C, seems to rule out any dissociative mechanism and favours a sterically controlled olefin rotation process. In this compound, hindrance to rotation arises from steric interaction between the bulky $NCMe_3$ group and the CO_2Me olefinic substituent. With less sterically demanding imino nitrogen and/or olefinic substituents, an AB pattern is observed at −70 °C for [Pd(ma)(C_5H_4N-2-CH=$NCMe_3$)] [δ_H 3.88, ^3J(HH) 3.9 Hz], whereas for [Pd(fn)-(C_5H_4N-2-CH=NMe)] the olefinic proton resonance is detected as a singlet even at the lowest temperature employed (−90 °C, δ_H 2.80).

Kinetic Studies.—The mechanism of reaction (1) was investigated by kinetic measurements of the rates of phenylation of the cationic substrates [Pd(η^3-2-$R^1C_3H_4$)(N-N')]ClO_4 by $NaBPh_4$ in the presence of activated olefins, under pseudo-first-order conditions, in aqueous (2% v/v) methanol at 25 °C. The results are summarized in Table 3.

A preliminary account of such a study has already appeared.[11] Abstract factor analysis of UV-VIS spectral changes in the range 500–300 nm indicated the presence of only two absorbing species, namely the cationic palladium(II) complex and the final palladium(0) product.[12] The infinity-time spectrum is superimposable with that of an authentic sample of the corresponding product under the same conditions. Experimentally $k_{obs} = k_1$, where k_{obs} is the pseudo-first-order rate constant determined by non-linear fitting of absorbance (A) *vs.* time data to the standard monoexponential law $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}\,t)$.[13]

The rate appears to be independent of both $NaBPh_4$ and olefin concentration, and is also independent of the nature of the olefin and of the ionic strength up to 0.003 mol dm^{-3} ($LiClO_4$). On the basis of conductivity measurements, ^1H NMR data and GC–MS experiments (see below), we propose the mechanism shown in Scheme 1, which involves rapid and extensive association between the cationic substrate and the BPh_4^- anion followed by slow, rate-determining, phenyl transfer to yield a labile intermediate [Pd(2-$R^1C_3H_4$)Ph(N-N')]. This subsequently undergoes rapid reductive allyl–phenyl coupling to form an allylbenzene, which is displaced immediately by the activated olefin to stabilize the ensuing palladium(0) product.

The corresponding rate law takes the general form of equation (2), which reduces to the observed behaviour $k_{obs} = k_1$

$$k_{obs} = k_1K_{eq}[BPh_4^-]/(1 + K_{eq}[BPh_4^-]) \qquad (2)$$

when $K_{eq}[BPh_4^-] \gg 1$. As can be seen, the rate data in Table 3 are fully consistent with the reactivity trends reported earlier under preparative conditions.

Cation–Anion Association Equilibrium (K_{eq}).—The large extent of ion pairing between the cationic substrates and BPh_4^- is confirmed by the high values of the association equilibrium constant K_{eq} in absolute methanol at 25 °C for the complexes [Pd(η^3-2-MeC_3H_4)(tmen)]BPh_4 (tmen = *N,N,N',N'*-tetramethylethylenediamine) and [Pt(η^3-2-MeC_3H_4)(C_5H_4N-2-CH=NC_6H_4OMe-4)]BPh_4, which do not undergo the phenyl transfer reaction (1). The Fuoss–Shedlovsky treatment of molar conductivity *vs.* concentration data yields K_{eq} values of 2950 ± 80 and 14 500 ± 400 dm^3 mol^{-1} for the palladium and platinum derivatives, respectively.[14] Such association cannot be detected by UV-VIS spectroscopy since the initial spectra of [Pd(η^3-2-$R^1C_3H_4$)(N-N')]BPh_4 and of the corresponding cationic complexes with ClO_4^- as the counter anion are virtually superimposable at comparable concentrations. Moreover, addition of an excess of $NaBPh_4$ to a methanolic solution of the cationic substrates causes no appreciable changes in their time-zero electronic spectra.

The specific interaction of BPh_4^- anion with the cationic complexes is clearly borne out by the ^1H NMR data of Table 4.

When the counter anion is changed from ClO_4^- to BPh_4^- in CD_2Cl_2, a general upfield shift of the proton resonances is observed, with the N=CH imino and H^3 2-pyridyl protons being most affected. The shielding of the latter protons decreases with increasing steric requirements of the imino nitrogen substituent in the compounds [Pd(η^3-2-$R^1C_3H_4$)(C_5H_4N-2-CH=NR^2)]X. This behaviour can be reasonably explained by the shielding effect of the phenyl ring currents of BPh_4^- in a tight ion pair[4] (as shown in Scheme 1), in which the cation–anion approach essentially depends on the steric requirements of the α-diimino ligand. Consistently, with more sterically demanding N-N' ligands, such as 4-$MeOC_6H_4N$=C(Me)-C(Me)=NC_6H_4OMe-4 and phen, the shielding influence of BPh_4^- is reduced markedly. On the other hand, in more polar and more co-ordinating solvents, such as CD_3CN and $(CD_3)_2CO$, the BPh_4^- shielding almost disappears since a closer cation–anion approach is hampered by the more extensive ion solvation and also by solvent co-ordination to the d^8 metal centre. Unfortunately, the low solubility of the complexes in CD_3OD prevented the recording of ^1H NMR spectra in this solvent. However, progressive addition of CD_3OD to a CD_2Cl_2 solution of [Pd(η^3-2-MeC_3H_4)(C_5H_4N-2-CH=NC_6H_4OMe-4)]BPh_4

Table 4 Hydrogen-1 NMR data for [M(η^3-2-R^{1}C$_3$H$_4$)(N–N′)]X complexes[a]

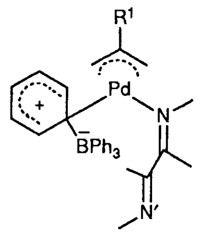
Compound	R^1	R^2	X$^-$	Solvent	Imino protons N=CH	2-Pyridyl protons H^3	H^4	H^5	H^6	N–R protons	Allyl protons H$_{syn}$	H$_{anti}$	R^1
[Pd(η^3-2-R^{1}C$_3$H$_4$)-{R^{2}N=C(Me)–C(Me)=NR^2}]	Me	C$_6$H$_4$OMe-4	ClO$_4$	CD$_2$Cl$_2$	2.32(s)[b]					3.82(s)[c]	3.17(s)	3.01(s)	2.01(s)
	Me	C$_6$H$_4$OMe-4	BPh$_4$	CD$_2$Cl$_2$	2.04(s)[b]					3.84(s)[c]	3.22(s)	2.99(s)	2.02(s)
[Pd(η^3-2-R^{1}C$_3$H$_4$)-(C$_5$H$_4$N-2-CH=NR^2)]X	Me	C$_6$H$_4$OMe-4	ClO$_4$	CD$_2$Cl$_2$	8.78(s)	8.22(m)	8.18(m)	7.78(m)	8.83(m)	3.85(s)[c]	3.95(s)	3.37(s)	2.19(s)
				CD$_3$CN	8.72(s)	8.06(m)	8.26(m)	7.74(m)	8.83(m)	3.85(s)[c]	3.99(s)	3.37(s)	2.17(s)
	Me	C$_6$H$_4$OMe-4	BPh$_4$	CD$_2$Cl$_2$	7.87(s)	<7.5[d]	7.88(m)	<7.5[d]	8.43(m)	3.85(s)[c]	3.80(s,br)	3.24(s)	2.15(s)
				CD$_3$CN	8.61(s)	7.95(m)	8.19(m)	7.68(m)	8.87(m)	3.85(s)[c]	3.97(s)	3.33(s)	2.15(s)
				(CD$_3$)$_2$CO	8.93(s)	8.18(m)	8.34(m)	7.82(m)	8.97(m)	3.88(s)[c]	4.14(s)	3.48(s)	2.23(s)
	H	Me	ClO$_4$	CD$_2$Cl$_2$	8.70(q), ^4J(HMe) 1.7	8.05(m)	8.20(m)	7.71(m)	8.73(m)	3.90(d)[e]	4.25(d), ^3J(HR^1) 7.1	3.42(d, br), ^3J(HR^1) 13.0	5.85(m)
	H	Me	BPh$_4$	CD$_2$Cl$_2$	<7.5[d]	<7.5[d]	7.83(m)	<7.5[d]	8.32(m)	3.47(d)[e] ^4J(HMe) 1.7	4.02(d), ^3J(HR^1) 7.1	3.19(d), ^3J(HR^1) 12.9	5.65(m)
	H	CMe$_3$	ClO$_4$	CD$_2$Cl$_2$	8.59(s)	8.07(m)	8.23(m)	7.70(m)	8.74(m)	1.46(s)[f]	4.38(d), ^3J(HR^1) 7.1	3.47(d), ^3J(HR^1) 12.6	5.83(m)
	H	CMe$_3$	BPh$_4$	CD$_2$Cl$_2$	8.14(s)	<7.5[d]	7.85(m)	<7.5[d]	8.28(m)	1.38(s)[f]	4.16(d), ^3J(HR^1) 7.1	3.28(d), ^3J(HR^1) 12.6	5.65(m)
[Pt(η^3-2-R^{1}C$_3$H$_4$)-(C$_5$H$_4$N-2-CH=NR^2)]X	Me	C$_6$H$_4$OMe-4	ClO$_4$	CD$_2$Cl$_2$	9.34(s), ^3J(PtH) 72.5	8.40(m)	8.28(m)	7.77(m)	9.10(m), ^3J(PtH) 34.0	3.86(s)[c]	3.94(m), ^2J(PtH) 26.0 3.56(m), ^2J(PtH) 28.0	3.03(m), ^2J(PtH) 74.0 2.88(m), ^2J(PtH) 76.0	2.30(s), ^3J(PtH) 84.2
	Me	C$_6$H$_4$OMe-4	BPh$_4$	CD$_2$Cl$_2$	7.92(s), ^3J(PtH) 73.0	<7.5[d]	7.84(m)	<7.5[d]	8.71(m), ^3J(PtH) 34.0	3.87(s)[c]	3.74(m), ^2J(PtH) 26.0 3.46(m), ^2J(PtH) 26.0	2.91(m), ^2J(PtH) 74.0 2.79(m), ^2J(PtH) 74.0	2.26(s), ^3J(PtH) 84.3
				CD$_3$CN	9.03(s), ^3J(PtH) 73.0	7.99(m)	8.24(m)	7.71(m)	9.06(m), ^3J(PtH) 34.0	8.35(s)[c]	3.98(m), ^2J(PtH) 26.0 3.55(m), ^2J(PtH) 26.0	2.99(m), ^2J(PtH) 74.0 2.85(m), ^2J(PtH) 74.0	2.27(s), ^3J(PtH) 84.5
						1,10-Phenanthroline protons							
						H^5,H^6	H^4,H^7	H^3,H^8	H^2,H^9				
[Pd(η^3-2-R^{1}C$_3$H$_4$)(phen)]X	H		ClO$_4$	CD$_2$Cl$_2$		8.11(s)	8.71(dd), ^3J(HH) 8.3, ^4J(HH) 1.5	7.99(dd), ^3J(HH) 4.9,	9.14(dd)		4.46(d), ^3J(HR^1) 7.1	3.66(d), ^3J(HR^1) 12.4	5.99(m)
	H		BPh$_4$	CD$_2$Cl$_2$		7.97(s)	8.51(dd), ^3J(HH) 8.3, ^4J(HH) 1.5	7.74(dd), ^3J(HH) 4.9	8.81(dd)		4.24(d), ^3J(HR^1) 7.2	3.47(d), ^3J(HR^1) 12.5	5.89(m)

[a] See footnote *a* in Table 2; the spectra of BPh$_4^-$ derivatives were recorded immediately after dissolution. [b] N=C–Me protons. [c] Methyl protons of the NC$_6$H$_4$OMe-4 group. [d] Masked by the phenyl proton resonances of BPh$_4^-$ anion in the range δ 7.5–6.7. [e] N–Me protons. [f] N–CMe$_3$ protons.

causes a progressive lowfield shift of the N=CH and H^3 signals towards the values observed for the corresponding perchlorate in CD_2Cl_2. In conclusion, formation of looser ion pairs in more polar and co-ordinating solvents results in a decreased association constant K_{eq} {*cf.* the K_{eq} values of 6990 ± 50 and 2950 ± 80 $dm^3 mol^{-1}$ for $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(tmen)]BPh_4$ in CH_2Cl_2 and MeOH, respectively} and in a decreased rate of phenylation. The observed solvent effect on the rate of reaction (1), reported earlier, can be interpreted in terms of a balance between solvating properties (as related to the relative permittivity) and co-ordinating ability of the solvent. Thus, in acetonitrile, which has both a high relative permittivity and co-ordinating ability, the reaction is slowed down to such an extent as to prevent any kinetic measurement.

Phenyl Transfer Step (k_1).—The transfer of a phenyl group from BPh_4^- to the allyl moiety may occur through different mechanisms. A radical pathway, initiated by a single electron-transfer process between the ionic species, is ruled out since addition of an efficient radical scavenger, such as cyclohexa-1,4-diene,[15] does not appreciably affect the reaction rates. Direct phenyl transfer to the η^3-bound allyl group seems unlikely, as it can hardly explain the lack of reactivity with $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(tmen)]BPh_4$ or $[Pt(\eta^3\text{-}2\text{-}MeC_3H_4)(C_5H_4N\text{-}2\text{-}CH{=}NC_6H_4OMe\text{-}4)]BPh_4$. On the other hand, the reaction of $[PdCl(\eta^3\text{-}2\text{-}R^1C_3H_4)L]$ (L = triarylphosphine or $AsPh_3$) with strong phenylating agents, such as LiR′ (R′ = aryl), yields the palladium–aryl derivatives $[PdR'(\eta^3\text{-}2\text{-}R^1C_3H_4)L]$, which subsequently undergo reductive elimination of allylbenzenes.[16] The ability of the BPh_4^- anion to transfer phenyl groups to d^8 metal centres of palladium(II) and platinum(II) complexes with weakly co-ordinating ligands is well documented.[17] Palladium(II)-co-ordinated ligands, such as isocyanides[18] and diolefins,[19] are also phenylated by BPh_4^-, allegedly through the intermediacy of a Pd–Ph transient species. In our case, we also propose that the phenyl transfer to the allyl moiety takes place *via* a labile intermediate $[Pd(2\text{-}R^1C_3H_4)Ph(N\text{-}N')]$, originating in the rate-determining step (k_1) through a Wheland-type electrophilic attack by the positive metal centre on a phenyl group of the BPh_4^- anion.[20]

The rate dependence of reaction (1) on the nature of α-diimine appears to parallel that observed for exchange between free and co-ordinated N–N′ in $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{-}N')]^+$ complexes, *i.e.* $R^2N{=}CH\text{-}CH{=}NR^2 > C_5H_4N\text{-}2\text{-}CH{=}NR^2 >$ bipy for $R^2 = C_6H_4OMe\text{-}4$, as determined from variable-temperature ^1H NMR spectra. This trend is better interpreted by assuming a transition state with a monodentate *N*-bonded α-diimine **II**.



II

Such a co-ordination mode with an *E-s-trans-E* α-diimine skeleton conformation has already been reported for d^8 metal complexes,[21] and is commonly assumed in the activation processes of ligand substitution reactions.[9,22] This transition state will also account for the fast *syn-syn,anti-anti* exchange of allylic protons detected in the ^1H NMR spectra of $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(C_5H_4N\text{-}2\text{-}CH{=}NR^2)]^+$ in the course of reaction (1). In contrast, no $\eta^3 \rightleftharpoons \sigma$ allyl conversion is observed to occur at any appreciable rate.

Consistently, the phenylation rates appear to be controlled by the π-accepting ability of the α-diimine (as it affects the electrophilic character of the metal centre), and by the tendency of the ligand to take on the *N* monodentate co-ordination mode. The latter increases with decreasing stability towards Pd–N bond breaking in the $\overline{\text{Pd–N–N}'}$ ring, and with decreasing steric requirements of imino carbon substituents.[21] The phenylation rate drops dramatically with the rigid phen ligand, and becomes negligible for $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(tmen)]^+$ or $[Pt(\eta^3\text{-}2\text{-}MeC_3H_4)(C_5H_4N\text{-}2\text{-}CH{=}NC_6H_4OMe\text{-}4)]^+$ substrates. For these two compounds, no exchange between free and co-ordinated tmen or $C_5H_4N\text{-}2\text{-}CH{=}NC_6H_4OMe\text{-}4$, respectively, is found to occur in the ^1H NMR spectra, indicating the presence of quite strong metal–nitrogen bonds. Accordingly, in the ^1H NMR spectrum of $[Pt(\eta^3\text{-}2\text{-}MeC_3H_4)(C_5H_4N\text{-}2\text{-}CH{=}NC_6H_4OMe\text{-}4)]BPh_4$ (see Table 4), the *syn-syn,anti-anti* allylic proton exchange does not take place at a detectable rate, at variance with the corresponding palladium(II) complex under comparable conditions. The above transition state **II** also agrees with the fact that reaction (1) is slowed down in solvents of good co-ordinating properties, or in the presence of Cl^- ions and free α-diimine, which can compete with BPh_4^- for the palladium(II) centre.

Recently, Venanzi and co-workers[5] have described the reaction of $BR'_4{}^-$ (R′ = aryl) with the cationic disolvento complexes *cis*-$[Pt(ROH)_2L_2]^{2+}$ (R = H or Me), which yields the platinum–aryl derivatives *trans*-$[PtR'(ROH)L_2]^+$. They showed the arylating agent to be BR'_3, formed by fast proton transfer from the co-ordinated protic solvent to the $BR'_4{}^-$ anion. The proposed mechanism involves the intermediacy of an alkoxo-bridged $Pt\text{-}OR\text{-}BR'_3$ species. A similar mechanism for reaction (1) in aqueous MeOH, starting from five-co-ordinated solvento species[4] is not in agreement with our experimental evidence. The electrical conductivity of the system $[Pd(\eta^3\text{-}2\text{-}R^1C_3H_4)(N\text{-}N')]BPh_4$–olefin in MeOH does not fall off immediately to a negligible value, but decays at measurable rates, depending on the nature of N–N′. According to the above alternative mechanism benzene would be produced immediately, followed by slow formation of allylbenzenes up to a final 1 : 1 molar ratio. By contrast, GC–MS analysis of the reaction mixture $[Pd(\eta^3\text{-}C_3H_5)(C_5H_4N\text{-}2\text{-}CH{=}NC_6H_4OMe\text{-}4)]BPh_4$–dmf (1 : 1.2) in $EtOH\text{-}CH_2Cl_2$ (1 : 1 v/v) shows that benzene is formed at a lower rate and in a lesser amount than allylbenzene. The allylbenzene : benzene molar ratio is *ca.* 1 : 0.2 after 1 h from dissolution of the reactants, when the phenylation reaction is complete on the basis of electrical conductivity and UV–VIS spectral changes, and is *ca.* 1 : 0.25 after 2 h. This benzene actually originates from slow interaction of the protic solvent with BPh_3,[23] produced in the course of reaction (1), as is also confirmed by GC–MS analysis of an ethanolic solution of BPh_3. Incidentally, GC–MS analysis of the products of reaction (1) in EtOH or in $EtOH\text{-}CH_2Cl_2$ (1 : 1 v/v) rules out any formation of allyl ethyl ether, which might arise from reductive ethoxo-allyl coupling in the alleged palladium-alkoxo intermediates.[24]

Experimental

The allylic chloro-bridged dimers $[\{MCl(\eta^3\text{-}2\text{-}R^1C_3H_4)\}_2]$ (M = Pd, R^1 = H or Me; M = Pt, R^1 = Me) and the α-diimines $R^2N{=}CH\text{-}CH{=}NR^2$ ($R^2 = C_6H_4OMe\text{-}4$ or CMe_3), $R^2N{=}C(Me)\text{-}C(Me){=}NR^2$ ($R^2 = C_6H_4OMe\text{-}4$), $C_5H_4N\text{-}2\text{-}CH{=}NR^2$ ($R^2 = C_6H_4OMe\text{-}4$, Me, or CMe_3) were prepared by published methods.[25,26] 1,2-Dichloroethane was distilled over anhydrous K_2CO_3 under nitrogen. All other chemicals and solvents were reagent grade, and were used without further purification. The phenylation reactions were carried out with magnetic stirring, and without special precautions against light or atmospheric moisture and oxygen, unless otherwise stated. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

Preparations.—[Pd(η^3-2-R^{1}C$_3$H$_4$)(N–N′)]ClO$_4$ (*N–N′ = α-diimine or tmen*).—These complexes were prepared by published procedures,[4,8] which involve reaction of [{PdCl(η^3-2-R^{1}C$_3$H$_4$)}$_2$] with the ligand N–N′ (1:2 molar ratio) in CH_2Cl_2, followed by addition of an excess of $NaClO_4 \cdot H_2O$ dissolved in MeOH (yields in the range 75–90%). The cationic derivatives [Pd(η^3-C$_3$H$_5$)(N–N′)]ClO$_4$ (N–N′ = C$_5$H$_4$N-2-CH=NCMe$_3$, bipy or phen) were prepared by treating [{PdCl(η^3-C$_3$H$_5$)}$_2$] (0.183 g, 0.5 mmol) with 1 mmol of N–N′ in MeOH (40 cm^3). After dissolution of the solids, dropwise addition of $NaClO_4 \cdot H_2O$ (0.28 g, 2 mmol) dissolved in water (10 cm^3) caused the precipitation of the products, which were filtered off, washed repeatedly with water and then with MeOH, and dried *in vacuo* (yields in the range 80–90%).

[M(η^3-2-R^{1}C$_3$H$_4$)(N–N′)]BPh$_4$ (M = Pd *or* Pt; N–N′ = *α-diimine or tmen*). These complexes were prepared by the published method for [Pd(η^3-2-MeC$_3$H$_4$)(C$_5$H$_4$N-2-CH=N-C$_6$H$_4$OMe-4)]BPh$_4$,[4] which involves reaction of [{MCl(η^3-2-R^{1}C$_3$H$_4$)}$_2$] with N–N′ (1:2 molar ratio) in MeOH at room temperature, followed by addition of NaBPh$_4$ (Pd:B 1:1) dissolved in MeOH–water (yields in the range 86–92%). Trace amounts of unreacted N–N′ ligand were removed from the dried products by repeated washing with Et$_2$O. This procedure is not viable when M = Pd and N–N′ = R^{2}N=CH–CH=NR^2 (R^2 = C$_6$H$_4$OMe-4 or CMe$_3$) owing to the high rate of phenyl transfer in the products, even in the solid state at low temperatures (−20 to 0 °C).

The complex [Pd(η^3-C$_3$H$_5$)(C$_5$H$_4$N-2-CH=NC$_6$H$_4$OMe-4)]BPh$_4$ is more conveniently prepared at about 0 °C to prevent its subsequent decomposition through phenyl transfer in the solid. The complex [Pd(η^3-2-MeC$_3$H$_4$){R^{2}N=C(Me)–C(Me)=NR^2}]BPh$_4$ (R^2 = C$_6$H$_4$OMe-4) is better prepared from reaction of [{PdCl(η^3-2-MeC$_3$H$_4$)}$_2$] (0.197 g, 0.5 mmol) with the appropriate α-diimine (0.296 g, 1 mmol) in CH$_2$Cl$_2$–MeOH (1:1 v/v; 60 cm^3), due to the low ligand solubility in MeOH. Prior to addition of NaBPh$_4$, the more volatile CH$_2$Cl$_2$ solvent was removed on a rotary evaporator. All the palladium derivatives were stored in the cold.

[Pd(olefin)(N–N′)]. *Method* (*a*). The cationic complex [Pd(η^3-2-R^{1}C$_3$H$_4$)(N–N′)]ClO$_4$ (0.5 mmol) [N–N′ = R^{2}N=CH–CH=NR^2 (R^2 = C$_6$H$_4$OMe-4 or CMe$_3$), or C$_5$H$_4$N-2-CH=NC$_6$H$_4$OMe-4] dissolved in acetone (50 cm^3) was treated with NaBPh$_4$ (0.171 g, 0.5 mmol) and the required olefin (fn or dmf, 0.6 mmol) at 25 °C. Upon completion, the solvent was evaporated to a small volume (*ca.* 5 cm^3), and MeOH (*ca.* 20 cm^3) was added to complete the precipitation of the product. After removal of the residual acetone at reduced pressure, the solid was filtered off, washed four times with MeOH and eventually with Et$_2$O. The compounds [Pd(olefin)(R^{2}N=CH–CH=NR^2)] [R^2 = C$_6$H$_4$OMe-4; olefin = dmf (wine-red) or fn (orange-brown)] required no further purification, whereas [Pd(dmf)(C$_5$H$_4$N-2-CH=NC$_6$H$_4$OMe-4)] was redissolved in CH$_2$Cl$_2$ in the presence of activated charcoal and free dmf (0.01 g). After filtration, the solution was concentrated and the pure orange product was recovered by precipitation with Et$_2$O. The more soluble complex [Pd(fn)(Me$_3$CN=CH–CH=N-CMe$_3$)] was isolated by taking the reaction mixture to dryness and treating the residue with CH$_2$Cl$_2$ and charcoal. After filtration, the pure product was precipitated from the solution as a yellow-green microcrystalline solid, as described above for [Pd(dmf)(C$_5$H$_4$N-2-CH=NC$_6$H$_4$OMe-4)].

Method (*b*). The cationic complex [Pd(η^3-2-R^{1}C$_3$H$_4$)(N–N′)]BPh$_4$ (0.5 mmol) [N–N′ = R^{2}N=C(Me)–C(Me)=NR^2 (R^2 = C$_6$H$_4$OMe-4), C$_5$H$_4$N-2-CH=NR^2 (R^2 = C$_6$H$_4$OMe-4, Me, or CMe$_3$), bipy or phen] dissolved in CH$_2$Cl$_2$ (50 cm^3) was treated with the required olefin (fn, dmf or ma, 0.6 mmol) at 30 °C. Upon completion, the solvent was evaporated to a small volume, and Et$_2$O was added to complete the precipitation. The crude products (some of which were contaminated by traces of metallic palladium) were redissolved in CH$_2$Cl$_2$ in the presence of charcoal and of a small amount of free olefin (*ca.* 0.05 mmol). The filtered solution was concentrated and then diluted with Et$_2$O to effect the precipitation of the pure palladium(0) compounds. The isolation of the more soluble complex [Pd(dmf)(C$_5$H$_4$N-2-CH=NCMe$_3$)] required a different procedure. On addition of Et$_2$O to the concentrated reaction mixture, a small amount of oily impurities separated. After treatment with charcoal and filtration, the solution was concentrated to induce initial precipitation of the product, which was completed by further dilution with Et$_2$O and storage in the cold (−20 °C) for 2 h.

The preparation of [Pd(fn)(phen)] was carried out at higher temperature (40 °C) to increase the reaction rate. The product was sparingly soluble in CH$_2$Cl$_2$ and precipitated during formation. At the end of the reaction Et$_2$O was added to complete the separation of the pale yellow complex which was not purified further.

Method (*c*). The allyl dimers [{PdCl(η^3-2-R^{1}C$_3$H$_4$)}$_2$] (0.5 mmol) were treated with bipy or C$_5$H$_4$N-2-CH=NR^2 (1 mmol; R^2 = C$_6$H$_4$OMe-4 or CMe$_3$), NaBPh$_4$ (0.342 g, 1 mmol) and the required olefin (1.2 mmol) in 1,2-dichloroethane (60 cm^3) at 50 °C, under nitrogen. The slightly soluble NaBPh$_4$ salt dissolved progressively upon reaction, while solid NaCl precipitated from the mixture. On completion, activated charcoal was added to adsorb the palladium metal arising from decomposition of the final products. This occurred to a larger extent in the case of C$_5$H$_4$N-2-CH=NCMe$_3$ derivatives. After filtration and concentration, Et$_2$O was added to precipitate the crude products, which were reprecipitated from 1,2-dichloroethane–diethyl ether, in the presence of a small amount of free olefin (*ca.* 0.1 mmol). The complex [Pd(dmf)(C$_5$H$_4$N-2-CH=NC$_6$H$_4$OMe-4)] appeared to be contaminated by BPh$_4^-$ containing impurities, even after repeated reprecipitations.

Attempted Isolation of BPh$_3$ *as a* 4-*Dimethylaminopyridine Adduct.*—Dimethyl fumarate (0.18 g, 1.2 mmol) was dissolved in CH$_2$Cl$_2$ (100 cm^3), and the solution was purged by bubbling nitrogen. The complex [Pd(η^3-2-MeC$_3$H$_4$)(C$_5$H$_4$N-2-CH=NC$_6$H$_4$OMe-4)]BPh$_4$ (0.69 g, 1 mmol) was added, and the resulting mixture was kept at 30 °C under nitrogen for 60 min. After concentration to a small volume, the palladium(0) product was precipitated by addition of degassed Et$_2$O and was filtered off. The filtrate was treated with 4-dimethylaminopyridine (4-dmapy) (0.15 g, 1.2 mmol) and charcoal. After filtration, the solvents were evaporated to leave an oily residue which solidified upon repeated washings with pentane. The whitish solid crystallized from a concentrated Et$_2$O solution after standing for 2 d at −20 °C under nitrogen. This compound (0.15 g) was identified as Ph$_2$(OH)B(4-dmapy) by elemental analysis (Found: C, 74.6; H, 6.9; N, 9.2. C$_{19}$H$_{21}$BN$_2$O requires C, 75.0; H, 6.95; N, 9.2%), IR spectra [ν(OH) at 3590 cm^{-1} (Nujol mull)], and ^{1}H NMR spectra in CD$_2$Cl$_2$ {4-dmapy protons: δ 8.21 (2 H, m, H^2 and H^6), 6.54 (2 H, m, H^3 and H^5) and 3.08 (6 H, s, NMe$_2$); phenyl protons: δ 7.5–7.0 (10 H, m, B–Ph)}.

Physical Measurements and Instrumentation.—The conductivity measurements were carried out with a CDM83 conductivity meter. The ^{1}H NMR spectra were recorded on a Varian FT80A spectrometer operating at 79.542 MHz. The IR spectra were recorded on a Perkin-Elmer 983G instrument, using Nujol mulls and CsI windows in the range 4000–200 cm^{-1}, and CaF$_2$ cells of 0.5 mm width for solution samples in the range 2500–1500 cm^{-1}. The solution electronic spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer, using quartz cells of 1 cm pathlength. Molecular weights were measured with a Knauer osmometer, in 1,2-dichloroethane at 32 °C. GC–MS analyses were carried out on a Carlo Erba AUTO/HRGC/MS QMD1000 instrument. The kinetics was followed by standard UV–VIS spectrophotometric techniques (500–300 nm) at 25 °C in a thermostatted cell compartment, for more than three half-lives. On prolonged standing, some decomposition to palladium metal occurred, affecting the accuracy of measurements. Statistical analysis of the experimental data was carried out as described elsewhere[13] on a IBM PS/2 50 personal computer equipped with an INTEL 80287 math coprocessor.

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