Cyclopalladiated Aromatic Imines in Organic Synthesis: The Preparation of Cinnamonitriles, Cinnamates, Unsymmetrical Stilbenes, Isoquinolones, and Isoquinolines[1]

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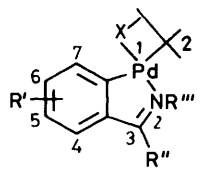
The preparation and characterisation of some new *ortho*-palladiated benzaldimine complexes and their reaction with olefins are described. The reaction of di-μ-1-chloro-bis(2-alkyl-2,1-benzazapalladole) complexes (**1**) with styrene in trifluoroacetic acid–acetic acid mixtures yielded stilbene-2-carbaldehydes (**10**). These were converted into 2-methyl-3-phenyl-1(2*H*)-isoquinolones (**12**) *via* a mercury(II) mediated cyclisation of the *N*-methylimine derivatives of the stilbenes. Reaction of the complexes (**1**) with methyl acrylate produced methyl 2-(*N*-t-butyliminomethyl)cinnamates (**7**; Y = CO_2Me) and with acrylonitrile, the 2-(*N*-t-butyliminomethyl)cinnamonitriles (**7**; Y = CN), which upon *in situ* thermolysis gave the corresponding isoquinolines (**8**).

The regiospecific substitution of functionalised aromatics *via* cyclometallated intermediates is a powerful synthetic tool[2] which is widely used for main group metals but although transition metal *ortho*-metallated complexes are well known, particularly those of palladium,[2,3] their potential in organic synthesis remains underexploited. Palladium is capable of mediating a wide range of carbon–carbon bond forming reactions[4] and the application of these to *ortho*-palladiated aromatics holds promise for novel and useful chemistry. Functionalisation *ortho* to a chelating group provides a direct route to fused ring systems[5] as in the carbonylation and isocyanide reactions of *ortho*-palladiated Schiffs bases (**1**), azobenzenes (**2**), and *N*,*N*-dialkylbenzylamines (**3**) to indazolones and phthalidimines.[6]



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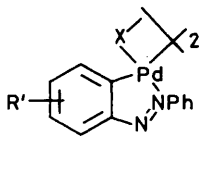

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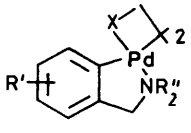

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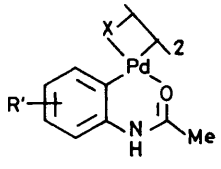

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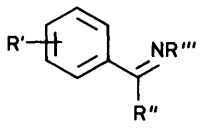


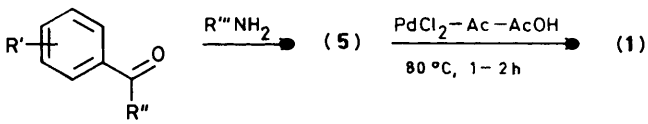
(5)

Similarly quinolines are produced by the reaction of the acetanilide complexes (**4**) with acrylaldehyde diethyl acetal.[7]

The extension of the above methodology to isoquinoline synthesis requires the use of a 2-carbon unit to react with the Schiffs base or benzylamine type complexes (**1**) or (**3**). Since the Schiffs base complexes are in the correct oxidation state for isoquinoline synthesis and the imino function is more synthetically versatile than the dimethylaminomethyl group we chose to operate on this system.

The *E*-imines (**5**) were prepared from the appropriate carbonyl compounds and amines by standard dehydration methods[8] and are listed in Table 1. The corresponding

Table 1. Synthesis of the imines (**5**) and the complexes (**1**)

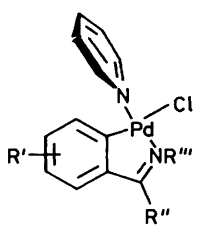


Compound	R′	R″	R‴	(5) (%)	(1) (%)
a	H	H	Me	86	82
b	H	H	Ph	93	92
c	H	H	Bu	88	91
d	H	H	Pr^i	98	94
e	H	H	Bu^t	72	95
f	H	Me	Bu	83	63
g	3,4-$(MeO)_2$	H	Bu^t	82	89[a]
h	2-MeO	H	Bu^t	78	81
i	3-MeO	H	Bu^t	84	96[b]
j	4-MeO	H	Bu^t	86	95
k	4-Me	H	Bu^t	79	89
l	4-Cl	H	Bu^t	79	88
m	4-Me_2N	H	Bu^t	73	—
n	4-O_2N	H	Bu^t	86	—

[a] Product: [**1**; R′ = 5,6-$(MeO)_2$, R″ = H, R‴ = Bu^t]. [b] Product: (**1**; R′ = 5-MeO, R″ = H, R‴ = Bu^t).

complexes (**1**), also listed in Table 1, were synthesized in generally good yields by treatment of the imines with palladium chloride in the presence of sodium acetate in acetic acid at 80 °C.

These dimeric complexes are yellow, air-stable, high melting crystalline solids with generally poor solubility in organic solvents but when split by ligands such as pyridine or triphenylphosphine, the resulting monomers (**6**) are usually freely soluble.



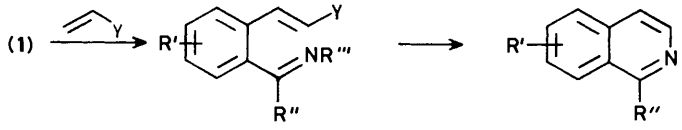
(6)

The lack of reactivity of the 4-nitroimine (**5n**) was not unexpected[9] but the 4-*N*,*N*-dimethylamino imine (**5m**) was expected to palladiate readily. In the event, although it reacted rapidly, a mixture of products resulted from which the *ortho*-palladiated complex could not be separated. Simple *N*,*N*-dialkylanilines have been reported to react abnormally with palladium(II)[10] and the enhanced reactivity of the imine cyclopalladiation clearly could not overcome this.

The low solubility of the complexes (**1**) meant that their n.m.r. spectra were best taken as the corresponding monomeric pyridine complexes (**6**) in [$^2H_5$]pyridine. In the complexes (**6**), 7-H lies in the shielding cone of the pyridine ring and is shifted by 1—2 p.p.m. to high field. The aromatic resonances are thereby simplified and the site of palladiation can be defined precisely, most importantly in those cases, *e.g.* complexes (**1i**) and (**1g**), where two potential sites are present.

Although palladiation of the imines (**5a**) and (**5b**) by a literature procedure[11] with palladium acetate followed by chloride ion displacement of the acetate ligands gave products (**1**) identical with those obtained previously, since our modified procedure proved to be more technically simple and more economical we used this in all other syntheses.

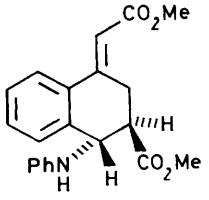
With the complexes to hand, the insertion of the two-carbon units was attempted. The primary reaction was the olefin insertion process[4] shown in Scheme 1.



Scheme 1.

Conceptually, the insertion of a vinyl ether or ester would give the correct functionality for direct access to the quinoline system. However, reports of the reaction of palladiated aromatics with vinyl ethers are rare[12] and in the event, reaction of (**1**) with butyl vinyl ether, vinyl acetate, or *N*-vinylpyrrolidine[13] in refluxing toluene under nitrogen and in the presence of triethylamine resulted only in a slow decomposition of the complex and no coupling. We therefore reverted to the standard Heck reactants, acrylates and styrenes.[4]

Reaction of the complex (**1**; R′ = R″ = H, R‴ = Ph) with an excess of methyl acrylate had been reported to give a double insertion product (**9**) *via* (**7**; R′ = R″ = H, R‴ = Ph, Y = CO_2Me) and the palladiated *N*,*N*-dialkylbenzylamine complexes (**3**) were known to react with acrylates and styrenes to give the *ortho*-substitution products.[14]



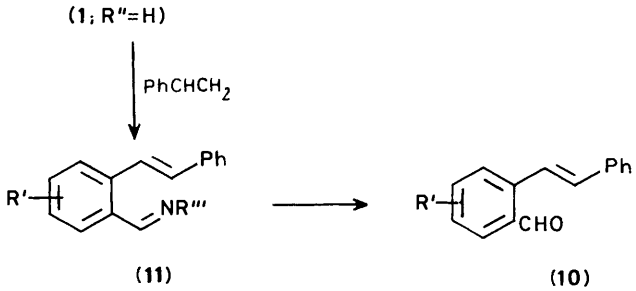
(**9**)

Accordingly, the complexes (**1**) were treated with styrene in trifluoroacetic acid–acetic acid under nitrogen at ambient temperature and after an aqueous work-up, the stilbene-2-carbaldehydes (**10**) were obtained in up to 91% yield (Table 2), the higher yields being produced with the *N*-t-butyl series. Only the *N*-methyl complex (**1a**) failed to react, with the order of reactivity being Bu^t > Pr^i > Bu > Me. Presumably, the bulkier the *N*-substituent the more facile the cleavage of the dimeric complex by the styrene and the more stable the complex with the olefin *cis* to the aryl residue as required for the insertion step. The n.m.r. spectra of the stilbenes (**10**) indicated the presence of only the *trans*-isomer. Although the effect of structural variation in the styrene was not studied, results in analogous reactions show a wide tolerance of the aryl ring functionality.[14]

This method allows the construction of a wide range of unsymmetrical *trans*-stilbene-2-carbaldehydes in a more direct and stereospecific manner than conventional routes.[15] These compounds are much used as precursors for heterocycles[16] and we considered that the corresponding *N*-methylimines (**11**; R‴ = Me), would provide a ready access to 3-arylquinolones (**12**) by an aminomercuriation process[17] (Scheme 2).

The aldehydes (**10**) were converted into their *N*-methylimines (**11**; R‴ = Me) and, without further purification were treated with mercuric acetate (2 equiv.) in refluxing toluene to produce the cyclised products (**12**) (Table 3). This cyclisation could, in principle, have given rise to 5- or 6-membered rings (see Scheme 2). However, the spectroscopic properties of the products (see

Table 2. Synthesis of *trans*-stilbene-2-carbaldehydes (**10**)



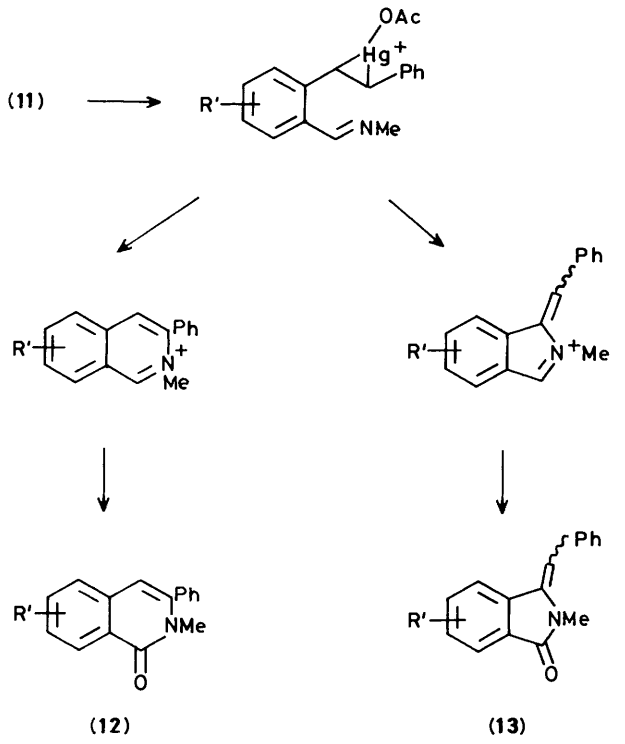
	Complex (**1**; R″ = H)		Stilbene (**10**)	
Compound	R′	R‴	R′	Yield (%)
a	H	Me	H	0
c	H	Bu	H	45
d	H	Pr^i	H	74
e	H	Bu^t	H	90[a]
g	5,6-$(MeO)_2$	Bu^t	4,5-$(MeO)_2$	91
h	4-MeO	Bu^t	3-MeO	67
i	5-MeO	Bu^t	4-MeO	81
j	6-MeO	Bu^t	5-MeO	75
k	6-Me	Bu^t	5-Me	74
l	6-Cl	Bu^t	5-Cl	85

[a] Reaction of (**1e**) with styrene in refluxing toluene in the presence of triethylamine gave the corresponding *N*-t-butylimine (**11**; R‴ = Bu^t) in 78% yield.

Table 3. Synthesis of 2-methyl-3-phenyl-1(2*H*)-isoquinolones (**12**)

	Stilbene (**10**)	Isoquinolone (**12**)	
Compound	R′	R′	Yield (%)[a]
a	H	H	43
g	4,5-$(MeO)_2$	6,7-$(MeO)_2$	62
h	3-MeO	8-MeO	33
i	4-MeO	7-MeO	32
j	5-MeO	6-MeO	59
l	5-Cl	6-Cl	41

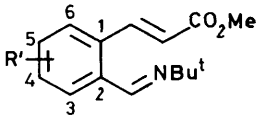
[a] Based on stilbenecarbaldehydes (**10**).



Scheme 2.

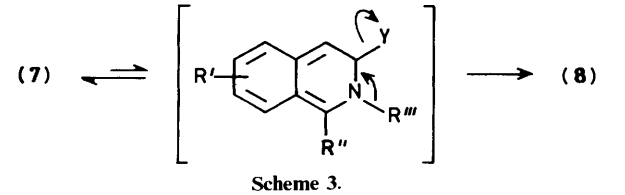
Experimental section) show clearly that the products were isoquinolones (**12**)[18] and not phthalimidines (**13**).[19] The use of 1 equiv. of oxidant did not allow the reaction to be stopped at the intermediate isoquinolinium ions, but simply gave half the yield of the isoquinolones (**12**).

The reaction of the *ortho*-palladiated *N*-t-butylimine complex (**1e**) with methyl acrylate was next attempted under the same acidic conditions as for the styrene reaction, but a multicomponent mixture containing only traces of methyl 2-formylcinnamate was produced. Consequently, the complex (**1e**) was refluxed under nitrogen, with an excess of methyl acrylate in toluene and in the presence of triethylamine to give the imine (**14a**) in 84% yield. Similarly prepared were (**14g**) (86%) and (**14k**) (79%). The latter was further hydrolysed with aqueous acetic acid to the corresponding aldehyde (**14k**; NBu^t = O) in 81% yield.



(**14**)

The concept for the final stages of Scheme 1 is shown in Scheme 3 and consists of an electrocyclic ring closure followed by loss of the groups R‴ and Y. This latter aromatisation step may be concerted.[20] For the overall process to be effective, the group Y must be a suitable leaving group and also be



Scheme 3.

Table 4. Synthesis of the isoquinolines (**8**)

	Stage 1		Stage 2		Isoquinoline (**8**)	
Compound	°C	h	°C	h	R′	Yield (%)[a]
(**1e**)	110	9	190—195	13	H	47
(**1g**)	100	12	180	8	6,7-(MeO)$_2$	10
(**1h**)	95	14[b]	—	—	—	—
(**1i**)	110	12	200	8	7-MeO	42
(**1j**)	110	8[b]	—	—	—	—
(**1k**)	100	12	190	12	6-Me	56
(**1l**)	110	8[b]	—	—	—	—

[a] Based on complexes (**1**). [b] The olefin insertion step did not occur.

compatible with the Heck-type reaction.[21] This role is fitted by the cyano group.

Thus treatment of the imine complex (**1e**) with acrylonitrile in the presence of triethylamine in refluxing toluene gave the nitrile adduct (**7e**; Y = CN) in 78% yield. This was heated in mesitylene at 160 °C to produce isoquinoline in 24% overall yield from (**1e**) together with hydrogen cyanide and 2-methylpropene. By using diphenyl ether–mesitylene (95:5) as solvent, the entire process could be carried out without isolation of the intermediate imine. Thus the complexes (**1**) were treated with an excess of acrylonitrile and triethylamine in the solvent mixture at 80—100 °C under nitrogen for 8—12 h. The excess of each reagent was removed under reduced pressure and the precipitated palladium and triethylamine hydrochloride were filtered off. The solution was then heated to 180—200 °C under nitrogen for a further 8—13 h. The results are given in Table 4.

In contrast to the styrene insertions, the reactions with acrylonitrile showed a pronounced substituent effect in the complexes (**1**). A π-donor substituent *para* to the palladium atom was necessary for an efficient insertion reaction. This can be rationalised as a balance of two major effects on the polarisation of the C–Pd bond important to the insertion process[22] with the electron-deficient acrylonitrile. A π-donor substituent *ortho* or *para* to the imino function will increase electron density on the nitrogen and hence the palladium atom, reduce the C–Pd polarisation, and reduce the nucleophilicity of the carbon atom, whereas a π-donor *para* to the C–Pd bond will increase the nucleophilicity of that carbon atom. These factors are clearly more important for the acrylonitrile insertion than for the styrene insertion.

The principal constraint on the chemistry described here is the cost of stoicheiometric amounts of palladium. Those transformations for which the reactants are not susceptible to oxidation by Pd^0/Pd^{II} oxidants (typically Cu^{II}/O$_2$) may be transformable into catalytic processes. This has yet to be developed, but within the above constraints the reactions provide a simple, rapid access to a range of functionalised heterocycles, some of which are not easily available by conventional syntheses.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus. Unless otherwise stated, i.r. spectra were recorded on a Perkin-Elmer 298 spectrometer, ^{1}H n.m.r. spectra on a Varian EM360A spectrometer and mass spectra on a V.G. Micromass 7070B spectrometer operating at 70 eV.

Chromatographic and crystallisation solvents were distilled before use and the THF and diethyl ether solvents used for organometallic reactions were freshly distilled from potassium–benzophenone. Toluene, mesitylene, and diphenyl ether were dried over and distilled from sodium. Acetic acid was purified by

a modification of the published procedure.[23] Thus the acid was warmed gently with acetic anhydride and chromium trioxide added *carefully* in small portions before the mixture was refluxed. Distillation gave the pure acid. All organometallic reactions were carried out under dry, oxygen-free nitrogen using degassed solvents.

General Preparation of Imines (**5**).—This was achieved by one of two methods.

(*a*) Equimolar amounts of the aldehyde and the amine were refluxed in benzene using a Dean and Stark trap to remove the calculated amount of water. The solvent was removed under reduced pressure and the product distilled or crystallised as appropriate.

(*b*) The aldehyde was stirred with 2 equiv. of the amine over 3A molecular sieves in ether and the reaction followed by i.r. spectroscopy.

Of the imines, (**5a**),[24] (**5b**),[25] (**5c**),[26] (**5d**),[24] (**5e**),[27] (**5f**),[28] (**5g**),[29] (**5j**),[30] (**5k**),[30] (**5l**),[30,31] (**5m**),[32] and (**5b**)[30] were all known and our products showed identical physical characteristics with those reported. Also synthesized (see Table 1) were the following.

N-(2-*Methoxybenzylidene*)-*t-butylamine* (**5h**). This was prepared by method (*b*) (78%), b.p. 102 °C/4.5 mmHg; $\nu_{max.}$(neat) 1 635 cm^{-1}; $\delta_H(CDCl_3)$ 8.67 (1 H, s), 7.9 (1 H, dd, *J* 7.8 and 2 Hz), 7.38—6.61 (3 H, m), 3.72 (3 H, s), and 1.25 (9 H, s); *m/z* 191 (M^+) (Found: C, 75.47; H, 9.05; N, 7.03. $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%).

N-(3-*Methoxybenzylidene*)-*t-butylamine* (**5i**). This was prepared by method (*b*) (84%), b.p. 144—146 °C/35 mmHg; $\nu_{max.}$(neat) 1 640 cm^{-1}; $\delta_H(CDCl_3)$ 8.26 (1 H, s), 7.4—6.8 (4 H, m), 3.82 (3 H, s), and 1.3 (9 H, s); *m/z* 191 (M^+) (Found: C, 75.1; H, 9.0; N, 7.25. $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%).

General Preparation of Complexes (**1**).—A magnetically stirred solution of anhydrous sodium acetate (15—20 equiv.) in acetic acid (80 ml, dry) was purged with nitrogen at 60 °C for 20—30 min. To this was added finely ground palladium chloride (0.708 g, 4 mmol) and the mixture purged for a further 10 min. The imine (**1**) (1.2—1.5 equiv.) was added, the temperature raised to 80 °C and the mixture stirred vigorously for a further 1—2 h until the solid palladium chloride had been replaced by a yellow precipitate and the brown colour of the supernatant was discharged. The mixture was cooled and diluted with water and the precipitate filtered off, washed with water, and air-dried. Recrystallisation of the product from THF–water or DMSO–water gave the complexes (**1**) as yellow crystalline solids. So prepared (see Table 1) were the known compounds (**1a**),[11] (**1b**),[11] and (**1e**).[33] Also synthesized were the following.

Di-μ-1-*chloro-bis*(2-*butyl*-2,1-*benzazapalladole*) (**1c**). Yellow crystals from THF–DMSO–H_2O (91%), m.p. 225—227 °C (darkening at 220 °C); $\nu_{max.}$(Nujol) 1 612 cm^{-1}; $\delta_H(CDCl_3)$ 7.9 (1 H, s), 7.85—6.7 (4 H, m), 3.5 (2 H, t, *J* 5 Hz), and 1.7—0.7 (7 H, m); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 8.0 (1 H, s), 7.8—6.9 (3 H, m), 6.35 (1 H, m), 3.91 (2 H, t, *J* 6.8 Hz), and 2.2—0.9 (7 H, m) (Found: C, 43.55; H, 4.65; Cl, 11.9; N, 4.55. $C_{22}H_{28}Cl_2N_2Pd_2$ requires: C, 43.74; H, 4.67; Cl, 11.74; N, 4.64%).

Di-μ-1-*chloro-bis*(2-*isopropyl*-2,1-*benzazapalladole*) (**1d**). Yellow crystals from THF–H_2O (94%), m.p. 240—241 °C (darkening at 230 °C); $\nu_{max.}$(Nujol) 1 605 cm^{-1}; $\delta_H(CDCl_3$–[$^2H_6$]DMSO) 8.05 (1 H, s), 7.8—6.85 (4 H, m), 4.2 (1 H, m), and 1.4 (6 H, d, *J* 6.2 Hz); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 8.0 (1 H, s), 7.4—6.7 (3 H, m), 6.13 (1 H, m), 4.6 (1 H, sept., *J* 6.1 Hz), and 1.4 (6 H, d, *J* 6.1 Hz) (Found: C, 41.95; H, 4.2; Cl, 12.25; N, 4.85. $C_{20}H_{24}Cl_2N_2Pd_2$ requires C, 41.7; H, 4.2; Cl, 12.3; N, 4.9%).

Di-μ-1-*chlorobis*(2-*butyl*-3-*methyl*-2,1-*benzazapalladole*) (**1f**). Yellow crystals from THF–H_2O (63%), m.p. 205—206 °C (decomp.); $\nu_{max.}$(Nujol) 1 600br cm^{-1}; $\delta_H(CDCl_3)$ 7.5—6.8 (4 H, m), 3.6 (2 H, m), 2.23 (3 H, s), and 2.1—0.8 (7 H, m); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 7.4—6.8 (3 H, m), 6.15 (1 H, m), 3.9 (2 H, t, *J* 6.5 Hz), 2.2 (3 H, s), and 2.0—0.8 (7 H, m) (Found: C, 45.4; H, 4.85; N, 4.45. $C_{24}H_{32}Cl_2N_2Pd_2$ requires C, 45.59; H, 5.10; N, 4.43%).

Di-μ-1-*chloro-bis*(5,6-*dimethoxy*-2-*t-butyl*-2,1-*benzazapalladole*) (**1g**). Yellow crystals from THF–H_2O (89%), m.p. 270—272 °C (darkening at 230—240 °C); $\nu_{max.}$(Nujol) 1 603 cm^{-1}; $\delta_H(CDCl_3)$ 7.98 (1 H, s), 7.23 (1 H, s), 7.0 (1 H, s), 4.05 (3 H, s), 3.98 (3 H, s), and 1.6 (9 H, s); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 7.9 (1 H, s), 6.96 (1 H, s), 5.46 (1 H, br s), 3.77 (3 H, s), 3.46 (3 H, s), and 1.64 (9 H, s) (Found: C, 43.35; H, 5.0; Cl, 10.0; N, 3.65. $C_{26}H_{36}Cl_2N_2O_4Pd_2$ requires C, 43.12; H, 5.01; Cl, 9.79; N, 3.87%).

Di-μ-1-*chloro-bis*(4-*methoxy*-2-*t-butyl*-2,1-*benzazapalladole*) (**1h**). Yellow crystals from THF–DMSO–H_2O (81%), m.p. > 300 °C (darkening at 250—265 °C); $\nu_{max.}$(Nujol) 1 595 cm^{-1}; $\delta_H(CDCl_3$–[$^2H_6$]DMSO) 8.2 (1 H, s), 7.4—6.4 (3 H, m), 3.82 (3 H, s), and 1.45 (9 H, s); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 8.29 (1 H, s), 6.82 (1 H, br t, *J* 7.5 Hz), 6.46 (1 H, br d, *J* 7.5 Hz), 5.45 (1 H, br d, *J* 7.5 Hz), 3.78 (3 H, s), and 1.62 (9 H, s) (Found: C, 43.55; H, 4.85; Cl, 10.75; N, 4.2. $C_{24}H_{32}Cl_2N_2O_2Pd_2$ requires C, 43.4; H, 4.86; Cl, 10.68; N, 4.22%).

Di-μ-1-*chloro-bis*(5-*methoxy*-2-*t-butyl*-2,1-*benzazapalladole*) (**1i**). Yellow crystals from THF–H_2O (96%), m.p. 254—256 °C (darkening at 195—215 °C); $\nu_{max.}$(Nujol) 1 607 cm^{-1}; $\delta_H(CDCl_3)$ 7.8 (1 H, s), 7.25 (1 H, d, *J* 2 Hz), 6.8—6.45 (2 H, m), 3.73 (3 H, s), and 1.53 (9 H, s); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 7.91 (1 H, s), 6.92 (1 H, d, *J* 3 Hz), 6.47 (1 H, dd, *J* 8.6 and 3 Hz), 5.82 (1 H, d, *J* 8.6 Hz), 3.65 (3 H, s), and 1.6 (9 H, s) (Found: C, 43.75; H, 4.9; Cl, 10.6; N, 4.15. $C_{24}H_{32}Cl_2N_2O_2Pd_2$ requires C, 43.40; H, 4.86; Cl, 10.68; N, 4.22%).

Di-μ-1-*chloro-bis*(6-*methoxy*-2-*t-butyl*-2,1-*benzazapalladole*) (**1j**). Yellow crystals from THF–H_2O (95%), m.p. 262 °C (darkening at 220—235 °C); $\nu_{max.}$(Nujol) 1 604 cm^{-1}; $\delta(CDCl_3)$ 7.68 (1 H, s), 7.15—6.94 (2 H, m), 6.34 (1 H, dd, *J* 8.4 and 2 Hz), 3.63 (3 H, s), and 1.33 (9 H, s); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 7.83 (1 H, s), 7.17 (1 H, d, *J* 8.2 Hz), 6.43 (1 H, dd, *J* 8.2 and 2.5 Hz), 5.36 (1 H, d, *J* 2.5 Hz), 3.42 (3 H, s), and 1.51 (9 H, s) (Found: C, 43.95; H, 2.9; Cl, 10.6; N, 4.2. $C_{24}H_{32}Cl_2N_2O_2Pd_2$ requires C, 43.40; H, 4.86; Cl, 10.86; N, 4.22%).

Di-μ-1-*chloro-bis*(6-*methyl*-2-*t-butyl*-2,1-*benzazapalladole*) (**1k**). Yellow crystals from ether (89%), m.p. 232—234 °C (decomp.); $\nu_{max.}$(Nujol) 1 604 cm^{-1}; $\delta_H(CDCl_3)$ 7.76 (1 H, s), 7.3—6.7 (3 H, m), 2.28 (3 H, s), and 1.51 (9 H, s); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 7.88 (1 H, s), 7.18 (1 H, d, *J* 7.5 Hz), 6.81 (1 H, br d, *J* 7.5 Hz), 5.7 (1 H, br s), 2.09 (3 H, s), and 1.64 (9 H, s) (Found: C, 45.55; H, 5.05; Cl, 11.4; N, 4.4. $C_{24}H_{32}Cl_2N_2Pd_2$ requires C, 45.59; H, 5.1; Cl, 11.22; N, 4.43%).

Di-μ-1-*chloro-bis*(6-*chloro*-2-*t-butyl*-2,1-*benzazapalladole*) (**1l**). Yellow crystals from THF–H_2O (88%), m.p. 282—284 °C (darkening at 240 °C); $\nu_{max.}$(Nujol) 1 604 cm^{-1}; $\delta_H(CDCl_3)$ 7.74 (1 H, s), 7.5—7.01 (3 H, m), and 1.57 (9 H, s); $\delta_H(CDCl_3$–[$^2H_5$]pyridine) 7.83 (1 H, s), 7.23 (1 H, d, *J* 8 Hz), 6.98 (1 H, dd, *J* 8 and 2 Hz), 5.87 (1 H, br s), and 1.64 (9 H, s) (Found: C, 39.6; H, 4.05; Cl, 20.35; N, 3.9. $C_{22}H_{26}Cl_4N_2Pd_2$ requires: C, 39.26; H, 3.90; Cl, 21.07; N, 4.16%).

General Preparation of Stilbene-2-*carbaldehydes* (**10**).—Styrene (2 ml, excess) was added over 10 min to a stirred suspension of the complex (**1**) (2 mmol) in trifluoroacetic acid–acetic acid (1:3, 35 ml) at 0—5 °C. The mixture was allowed to warm to room temperature after which stirring was continued for a further 24—36 h until the yellow suspension of the complex had been replaced by a deposit of palladium metal. The mixture was filtered and the filtrate diluted with water, neutralised (aq. Na_2CO_3), and the organic products extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and the solvent and excess of styrene evaporated. The residue was chromatographed over silica H60 [eluant light petroleum (b.p.

40—60 °C)–ether] to give the stilbene-2-carbaldehydes (**10**). Thus synthesized (see Table 2) were the following.

trans-*Stilbene-2-carbaldehyde* (**10a**). Colourless oil [45, 74, and 90% respectively from complexes (**1c**), (**1d**), and (**1e**)] (lit.,[15] m.p. 83 °C); spectroscopically consistent with the reported material (Found: C, 86.65; H, 6.0. Calc. for $C_{15}H_{12}O$: C, 86.51; H, 5.81%).

4,5-*Dimethoxy*-trans-*stilbene-2-carbaldehyde* (**10g**). Needles from light petroleum (b.p. 40—60 °C)–ether (91%), m.p. 150—151 °C; $\nu_{max.}$(Nujol) 1 670, 1 590, and 1 515 cm^{-1}; $\delta_H(CDCl_3)$ 10.3 (1 H, s), 7.85 (1 H, d, *J* 16 Hz), 7.6—7.15 (7 H, m), 6.85 (1 H, d, *J* 16 Hz), 3.95 (3 H, s), and 3.87 (3 H, s); *m/z* 268 (M^+) and 204 (100%) (Found: C, 75.9; H, 5.95. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.01%).

3-*Methoxy*-trans-*stilbene-2-carbaldehyde* (**10h**). Prisms from light petroleum (b.p. 40—60 °C)–ether (67%), double m.p. 120—121 °C and 124—125 °C; $\nu_{max.}$(Nujol) 1 675 and 1 565 cm^{-1}; $\delta_H(CDCl_3)$ 10.65 (1 H, s), 8.06 (1 H, d, *J* 16 Hz), 7.6—6.7 (9 H, m), and 3.76 (3 H, s); *m/z* 238 (M^+, 100%) (Found: C, 80.65; H, 5.95. $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.92%).

4-*Methoxy*-trans-*stilbene-2-carbaldehyde* (**10i**). Needles from light petroleum (b.p. 40—60 °C)–ether (81%), m.p. 59.5 °C; $\nu_{max.}$(Nujol) 1 675 and 1 595 cm^{-1}; $\delta_H(CDCl_3)$ 10.24 (1 H, s), 7.82 (1 H, d, *J* 16 Hz), 7.6—7.0 (8 H, m), 6.8 (1 H, d, *J* 16 Hz), and 3.72 (3 H, s); *m/z* 238 (M^+, 100%) (Found: C, 80.7; H, 5.95. $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.92%).

5-*Methoxy*-trans-*stilbene-2-carbaldehyde* (**10j**). Prisms from light petroleum (b.p. 40—60 °C)–ether (75%), m.p. 46—47 °C; $\nu_{max.}$(Nujol) 1 685, 1 600, and 1 550 cm^{-1}; $\delta_H(CDCl_3)$ 10.14 (1 H, s), 8.0 (1 H, d, *J* 16 Hz), 7.7—6.6 (9 H, m), and 3.8 (3 H, s); *m/z* 238 (M^+) and 105 (100%) (Found: C, 80.6; H, 5.95. $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.92%).

5-*Methyl*-trans-*stilbene-2-carbaldehyde* (**10k**). Colourless oil (74%); spectroscopic data consistent with the reported material.[34]

5-*Chloro*-trans-*stilbene-2-carbaldehyde* (**10l**). Needles from light petroleum (b.p. 40—60 °C)–chloroform (85%), m.p. 63—64 °C; $\nu_{max.}$(Nujol) 1 690 and 1 590 cm^{-1}; $\delta_H(CDCl_3)$ 10.1 (1 H, s), 7.83 (1 H, d, *J* 16 Hz), 7.67—7.04 (8 H, m), and 6.83 (1 H, d, *J* 16 Hz); *m/z* 242 (M^+, 100%), 207, and 178 (Found: C, 74.3; H, 4.6; Cl, 14.6. $C_{15}H_{11}ClO$ requires C, 74.23; H, 4.57; Cl, 14.61%).

2-(N-*t-Butyliminomethyl*)-trans-*stilbene* (**11e**).—Complex (**1e**) (1.5 mmol), styrene (2 ml), and triethylmine were refluxed together in toluene under nitrogen for 10 h. The precipitated palladium metal and triethylamine hydrochloride were filtered off and the solvent and excess of reagents evaporated to give the stilbene (**11a**) as an oil (78%), $\nu_{max.}$ 1 646 cm^{-1}; $\delta_H(CDCl_3)$ 8.6 (1 H, s), 8.1—7.0 (10 H, m), and 1.5 (9 H, s); *m/z* 263 (M^+), contaminated with the corresponding aldehyde (**10a**).

General Preparation of the N-*Methylimines* (**11**; R‴ = Me) *and the* 3-*Phenylisoquinolones* (**12**).—The imines (**11**; R‴ = Me) were synthesized as in method (*b*) above except that the solvent used was ethanol. On completion of the reaction (i.r. analysis), the solids were filtered off and the solvents removed under reduced pressure. The residual imines (**11**; R‴ = Me) were examined spectroscopically and then dissolved in toluene (to *ca.* 25mM), treated with mercuric acetate (2.2 equiv.), and the solution refluxed for 2—3 h. The mercury metal was removed and the toluene solution washed with water, dried (Na_2SO_4), and the solvent removed under reduced pressure. Chromatography over silica H60 [eluant light petroleum (b.p. 40—60 °C)–ether] gave the isoquinolones (**12**) which were further purified by recrystallisation as necessary. Thus synthesized were the following.

2-(N-*Methyliminomethyl*)-trans-*stilbene* (**11a**), $\nu_{max.}$(liq.) 1 650 cm^{-1}; $\delta_H(CDCl_3)$ 8.7 (1 H, d, *J* 2 Hz), 8.0—7.17 (10 H, m), 6.9 (1 H, d, *J* 16.5 Hz), and 3.54 (3 H, d, *J* 2 Hz) (Found: M^+, 221.1198. $C_{16}H_{15}N$ requires: *M*, 221.1183).

4,5-*Dimethoxy*-2-(N-*methyliminomethyl*)-trans-*stilbene* (**11g**; R‴ = Me), $\nu_{max.}$(liq.) 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 8.64 (1 H, d, *J* 2 Hz), 7.6—6.5 (9 H, m), 3.92 (3 H, s), 3.88 (3 H, s), and 3.51 (3 H, d, *J* 2 Hz); *m/z* 281 (M^+).

3-*Methoxy*-2-(N-*methyliminomethyl*)-trans-*stilbene* (**11h**; R‴ = Me), $\nu_{max.}$(liq.) 1 640 cm^{-1}; $\delta_H(CDCl_3)$ 8.74 (1 H, d, *J* 1.5 Hz), 7.96 (1 H, d, *J* 17 Hz), 7.6—6.65 (9 H, m), 3.72 (3 H, s), and 3.56 (3 H, d, *J* 1.5 Hz) (Found: M^+, 251.1308. $C_{17}H_{17}NO$ requires *M*, 251.1310).

4-*Methoxy*-2-(N-*methyliminomethyl*)-trans-*stilbene* (**11i**; R‴ = Me), $\nu_{max.}$(liq.) 1 645 cm^{-1}; $\delta_H(CDCl_3)$ 8.65 (1 H, d, *J* 1.7 Hz), 7.65—6.74 (9 H, m), 6.73 (1 H, d, *J* 16.5 Hz), 3.76 (3 H, s), and 3.49 (3 H, d, *J* 1.7 Hz) (Found: M^+, 251.1310. $C_{17}H_{17}NO$ requires *M*, 251.1310).

5-*Methoxy*-2-(N-*methyliminomethyl*)-trans-*stilbene* (**11j**; R‴ = Me), $\nu_{max.}$(liq.) 1 640 cm^{-1}; $\delta_H(CDCl_3)$ 8.5 (1 H, d, *J* 2 Hz), 7.85—6.65 (10 H, m), 3.74 (3 H, s), and 3.42 (3 H, d, *J* 2 Hz) (Found: M^+, 251.303. $C_{17}H_{17}NO$ requires *M*, 251.1310).

5-*Chloro*-2-(N-*methyliminomethyl*)-trans-*stilbene* (**11l**; R‴ = Me), $\nu_{max.}$(liq.) 1 635 cm^{-1}; $\delta_H(CDCl_3)$ 8.57 (1 H, d, *J* 2 Hz), 7.85—7.04 (9 H, m), 6.87 (1 H, d, *J* 16 Hz), and 3.5 (1 H, d, *J* 2 Hz).

2-*Methyl*-3-*phenyl*-1(2H)-*isoquinolone* (**12a**). Yield 43%, m.p. 65—68 °C [from light petroleum (b.p. 40—60 °C)] (lit.,[35] m.p. 68.5—70.5 °C); spectroscopically consistent with the reported material.

6,7-*Dimethoxy*-2-*methyl*-3-*phenyl*-1(2H)-*isoquinolone* (**12g**). Yield 62%, m.p. 232 °C (from ether–chloroform) (lit.,[35] m.p. 229—231 °C); spectroscopically consistent with the reported material (Found: C, 73.2; H, 5.85; N, 4.7. Calc. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74%).

8-*Methoxy*-2-*methyl*-3-*phenyl*-1(2H)-*isoquinolone* (**12h**). Yield 33%, m.p. 140—141 °C [from light petroleum (b.p. 40—60 °C)]; $\nu_{max.}$(Nujol) 1 650 cm^{-1}; $\delta_H(CDCl_3)$ 7.6—7.25 (6 H, m), 7.1—6.72 (2 H, m), 6.29 (1 H, s), 3.98 (3 H, s), and 3.35 (3 H, s); *m/z* 265 (M^+) (Found: C, 77.05; H, 5.45; N, 5.3. $C_{17}H_{15}NO_2$ requires C, 76.96; H, 5.7; N, 5.28%).

7-*Methoxy*-2-*methyl*-3-*phenyl*-1(2H)-*isoquinolone* (**12i**). Yield 32%, m.p. 137—139 °C [from light petroleum (b.p. 40—60 °C)–ether]; $\nu_{max.}$(Nujol) 1 644 cm^{-1}; $\delta_H(CDCl_3)$ 7.86 (1 H, d, *J* 2 Hz), 7.6—7.1 (7 H, m), 6.39 (1 H, s), 3.91 (3 H, s), and 3.42 (3 H, s); *m/z* 265 (M^+, 100%) (Found: C, 76.9; H, 5.7; N, 5.25. $C_{17}H_{15}NO_2$ requires: C, 76.96, H, 5.7; N, 5.28%).

6-*Methoxy*-2-*methyl*-3-*phenyl*-1(2H)-*isoquinolone* (**12j**). Yield 59%, m.p. 126—128 °C [needles from light petroleum (b.p. 40—60 °C)–ether]; $\nu_{max.}$(Nujol) 1 648 cm^{-1}; $\delta_H(CDCl_3)$ 8.39 (1 H, d, *J* 8 Hz), 7.45 (5 H, m), 7.04 (1 H, dd, *J* 8 and 2.5 Hz), 6.81 (1 H, d, *J* 2.5 Hz), 6.34 (1 H, s), 3.84 (3 H, s), and 3.40 (3 H, s); *m/z* 265 (M^+, 100%) (Found: C, 77.1; H, 5.75; N, 5.25. $C_{17}H_{15}NO_2$ requires: C, 76.96; H, 5.70; N, 5.28%).

6-*Chloro*-2-*methyl*-3-*phenyl*-1(2H)-*isoquinolone* (**12l**). Yield 41%, m.p. 150—151 °C [from light petroleum (b.p. 40—60 °C)–ether]; $\nu_{max.}$(Nujol) 1 640 cm^{-1}; $\delta_H(CDCl_3)$ 8.35 (1 H, d, *J* 9 Hz), 7.5—7.2 (7 H, m), 6.32 (1 H, s), and 3.41 (3 H, s); *m/z* 269 (M^+) (Found: C, 71.2; H, 4.5; Cl, 13.3; N, 5.2. $C_{18}H_{12}ClNO$ requires C, 71.25; H, 4.48; Cl, 13.14; N, 5.19%).

General Preparation of the Cinnamates (**14**).—The complexes (**1**) (1.5 mmol), methyl acrylate (2—3 ml, excess), and triethylamine (2—3 ml, excess) were refluxed under nitrogen for 10—24 h. When the complex had been consumed (discharge of the yellow colour), the precipitated metal and salts were filtered off and the solvent and excess of reagents removed under reduced pressure. The residues were distilled or crystallised as appropriate to give the pure cinnamates (**14**). Thus synthesized were the following.

Methyl 2-(N-*t-butyliminomethyl*)-trans-*cinnamate* (**14a**).

Yield 84%, b.p. 110—115 °C/0.04 mmHg; $\nu_{max.}$(liq.) 1 720 and 1 634 cm^{-1}; $\delta_H(CDCl_3)$ 8.56 (1 H, s), 8.42 (1 H, d, *J* 16.5 Hz), 7.9—7.1 (4 H, m), 6.27 (1 H, d, *J* 16.5 Hz), 3.77 (3 H, s), and 1.32 (9 H, s); *m/z* 245 (M^+) (Found: C, 73.4; H, 8.05; N, 5.7. $C_{15}H_{19}NO_2$ requires C, 73.44; H, 7.81; N, 5.71%).

Methyl 4,5-*dimethoxy*-2-(N-*t*-*butyliminomethyl*)-trans-*cinnamate* (**14g**). Yield 86%, m.p. 107 °C [needles from light petroleum (b.p. 40—60 °C)]; $\nu_{max.}$(Nujol) 1 710, 1 630, 1 590, and 1 510 cm^{-1}; $\delta_H(CDCl_3)$ 8.66 (1 H, s), 8.33 (1 H, d, *J* 16 Hz), 7.49 (1 H, s), 7.04 (1 H, s), 6.29 (1 H, d, *J* 16 Hz), 3.96 (3 H, s), 3.92 (3 H, s), 3.81 (3 H, s), and 1.35 (9 H, s); *m/z* 305 (M^+) (Found: C, 66.9; H, 7.85; N, 4.6. $C_{17}H_{23}NO_4$ requires: C, 66.86; H, 7.59; N, 4.59%).

Methyl 5-*methyl*-2-(N-*t*-*butyliminomethyl*)-trans-*cinnamate* (**14k**). Yield 79%, unstable yellow oil; $\nu_{max.}$(liq.) 1 712 and 1 628 cm^{-1}; $\delta_H(CDCl_3)$ 8.53 (1 H, s), 8.32 (1 H, d, *J* 16 Hz), 7.69 (1 H, d, *J* 7 Hz), 7.4—7.05 (2 H, m), 6.27 (1 H, d, *J* 16 Hz), 3.80 (3 H, s), 2.37 (3 H, s), and 1.32 (9 H, s); *m/z* 259 (M^+). In order to complete the characterisation, the imino function was hydrolysed with aqueous acetic acid during 16 h at room temperature to give *methyl* 2-*formyl*-5-*methylcinnamate* (**14k**; NBut = O) (81%), m.p. 60—60.5 °C [plates from light petroleum (b.p. 40—60 °C)–ether]; $\nu_{max.}$(Nujol) 1 710, 1 694, and 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 10.22 (1 H, s), 8.7 (1 H, d, *J* 16 Hz), 7.74 (1 H, d, *J* 7 Hz), 7.47—7.20 (2 H, m), 6.34 (1 H, d, *J* 16 Hz), 3.81 (3 H, s), and 2.45 (3 H, s); *m/z* 204 (M^+) (Found: C, 70.75; H, 5.9. $C_{12}H_{12}O_3$ requires: C, 70.68; H, 5.92%).

2-(N-*t*-*Butyliminomethyl*)-trans-*cinnamonitrile* (**7e**, Y = CN). Complex (**1e**) (1.5 mmol), acrylonitrile (2 ml, excess), and triethylamine (2 ml, excess) were refluxed in toluene under nitrogen until the reaction was complete (8 h). The precipitated metal and salts were filtered off and the solvent and excess of reagents removed under reduced pressure to give the *title compound* (**7e**; Y = CN) (78%); $\delta_H(CDCl_3)$ 8.46 (1 H, s), 8.28 (1 H, d, *J* 16.5 Hz), 7.75—7.1 (4 H, m), 5.7 (1 H, d, *J* 16.5 Hz), and 1.32 (9 H, s). This compound was used without further purification.

Isoquinoline (**8a**).—The crude nitrile (**7e**; Y = CN) was refluxed in mesitylene (40 ml) for 8 h after which the solution was diluted with water and acidified (dil. aq. HCl). The aqueous layer was separately washed with ether, basified (aq. NaOH), and the free bases extracted with ether. The ethereal layer was dried and the solvent removed under reduced pressure. Column chromatography of the residual oil over silica H60 [eluant light petroleum (b.p. 40—60 °C)–ether] gave the isoquinoline (**8a**) [24% from (**1e**)] spectroscopically identical with authentic material.

General Direct Preparation of the Isoquinolines (**8**).—Complex (**1**) (1.5 mmol), triethylamine (5 ml, excess), and acrylonitrile (5 ml, excess) were heated to 100—110 °C in diphenyl ether–mesitylene (95:5, 40—50 ml) for 9—12 h until the solution became colourless. The mixture was allowed to cool to room temperature when the precipitated metal and salts were filtered off. Excess of triethylamine and acrylonitrile were removed under reduced pressure and the resulting solution was heated at 180—200 °C for 8—13 h. The reaction was worked up as above and the isoquinolines purified by crystallisation. This technique gave the isoquinoline (**8a**) in 47% overall yield from (**1e**). Similarly synthesized were the following.

6,7-*Dimethoxyisoquinoline* (**8g**). Purified by chromatography over neutral alumina, yield 10%, m.p. 89—91 °C [from light petroleum (b.p. 40—60 °C)–ether] (lit.,[36] m.p. 90—91 °C); picrate m.p. 223—225 °C (yellow needles from ethanol) (lit.,[37] m.p. 226 °C).

7-*Methoxyisoquinoline* (**8i**). Yield 42%, m.p. 48—49 °C [from light petroleum (b.p. 40—60 °C)], (lit.,[38] m.p. 49 °C) (Found: C, 75.3; H, 5.7; N, 8.8. Calc. for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80%). Picrate, yellow crystals from EtOH, m.p. 203—205 °C (lit.,[38] m.p. 194—195 °C).

6-*Methylisoquinoline* (**8k**). Yield 56%, m.p. 85—87 °C [from light petroleum (b.p. 40—60 °C)] (lit.,[38] m.p. 83 °C), picrate m.p. 216 °C (yellow needles from ethanol) (lit.,[38] m.p. 212 °C).

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