# Complexes of the Platinum Metals. Part 43.[1] *N,N'*-Diphenylamidinato Derivatives of Ruthenium, Osmium and Iridium *

**Terry Clark and Stephen D. Robinson**
*Department of Chemistry, King's College London, Strand, London WC2R 2LS, UK*

*N,N'*-Diphenylamidines PhN=C(R)–NHPh (R = H, Me, Et or Ph) reacted with the precursors $[MH_2(CO)(PPh_3)_3]$, $[MH(Cl)(CO)(PPh_3)_3]$ and $[M(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot n$MeOH (M = Ru, *n* = 0.75; or Os *n* = 0.33) in boiling benzene to afford the amidinato complexes $[MH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$, $[MCl\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ and $[M(O_2CCF_3)\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ respectively. The hydrides $[MH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ have also been obtained by oxidative addition of amidines to $[Ru(CO)_3(PPh_3)_2]$ and by treatment of the precursors $[MH(Cl)(CO)(PPh_3)_3]$ with amidines in the presence of an excess of base ($NEt_3$). The trifluoroacetates $[M(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot n$MeOH reacted with amidines in the presence of $NEt_3$ to afford the hydrides $[MH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ (M = Ru, R = H; M = Os, R = H, Me, Et or Ph) or the bis(amidinato) complexes $[M\{PhNC(R)NPh\}_2(CO)(PPh_3)]$ (M = Ru; R = Me, Et or Ph). Reactions of the dichlorides $[MCl_2(PPh_3)_3]$ with amidines and base ($NEt_3$) in boiling toluene containing traces of alcohol were accompanied by a carbonyl-abstraction reaction leading to formation of $[MH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ and/or $[MCl\{PhNC(R)NPh\}(CO)(PPh_3)_2]$. The hydrides $[MH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ are also obtained when $[RuH_2(PPh_3)_4]$ or $[OsH_4(PPh_3)_3]$ reacts with amidines in boiling toluene (containing a trace of alcohol) or in 2-methoxyethanol. The carbonyl abstractions are remarkable in that they have no parallel in the corresponding reactions involving the related triazenide ($PhNNNPh^-$) and carboxylate ($RCO_2^-$) ligands even when neat alcohols are used as solvents. Reactions of *mer*-$[IrH_3(PPh_3)_3]$, $[IrHCl_2(PPh_3)_3]$–$NEt_3$ and $[IrHCl_2(PPh_3)_3]$ with amidines in boiling benzene or toluene afforded $[IrH_2\{PhNC(R)NPh\}(PPh_3)_2]$, $[IrH(Cl)\{PhNC(R)NPh\}(PPh_3)_2]$ and $[IrCl_2\{PhNC(Ph)NPh\}(PPh_3)_2]$ respectively.

As part of our study of small-ring chelates we have previously reported on the synthesis of triazenido chelates by the reactions of free diaryltriazenes, RNNNHR, with platinum-metal hydrides,[2,3] or with the corresponding chlorides and base ($NEt_3$).[4] We now describe parallel series of syntheses involving diphenylamidines PhNC(R)NHPh (R = H, Me, Et or Ph) leading to formation of an extensive range of amidinato chelates. Taken together these syntheses involving cleavage of triazene and amidine N–H bonds provide one of the most prolific examples of transition-metal-mediated N–H bond-breaking reactions reported to date.[5] The reactivity patterns displayed by the triazenes and amidines in these syntheses differ in that there is a marked tendency for the latter to promote concomitant carbonyl-abstraction reactions when carbonyl-free ruthenium and osmium precursors are employed. Some of the formamidinato complexes described herein have previously been prepared in this laboratory by the 1,2 insertion of carbodiimides RN=C=NR into metal–hydrogen bonds.[6,7] A preliminary report of the present work has appeared.[8]

## Experimental

Platinum-metal salts were supplied by Johnson Matthey plc and Inco(Europe) Ltd. The phosphine-containing ruthenium, osmium and iridium complex precursors were prepared by standard literature procedures.[9,10] The dihydrides $[MH_2(CO)(PPh_3)_3]$ (M = Ru or Os) were obtained by sodium tetrahydroborate reduction of the corresponding hydrochlorides $[MH(Cl)(CO)(PPh_3)_3]$ in boiling ethanol. *N,N'*-Diphenylbenzamidine, -acetamidine and -propionamidine were synthesised by litera ture methods.[11,12] *N,N'*-Diphenylformamidine was obtained from the Aldrich Chemical Company. All reactions were performed under a dinitrogen atmosphere using degassed solvents. Products were worked up in open flasks.

Elemental analyses were performed by the Microanalytical Laboratory at University College, London. Melting points were taken in sealed tubes under dinitrogen. Infrared spectra were recorded on a Perkin Elmer 983 G spectrometer using Nujol mulls, NMR spectra on Bruker AM 360 ($^1$H, 360.13, $^{13}$C-{$^1$H} 90.56 MHz, $SiMe_4$ as internal reference) and WM 250 spectrometers ($^{31}$P-{$^1$H} 101.26 MHz, 85% $H_3PO_4$ as external reference). Melting point and analytical data are recorded in Table 1, infrared and NMR data in Tables 2–4. Further $^{13}$C NMR data are available as supplementary material.

*Reactions involving* $[RuH_2(CO)(PPh_3)_3]$.—*Carbonyl*(N,N'-*diphenylformamidinato*)*hydridobis*(*triphenylphosphine*)*ruthenium*(II). A solution of $[RuH_2(CO)(PPh_3)_3]$ (0.15 g, 0.16 mmol) in benzene (10 $cm^3$) was brought to reflux with stirring. *N,N'*-Diphenylformamidine (0.14 g, 0.71 mmol) in ethanol (10 $cm^3$) was added and the mixture heated under reflux for 2 h. A second portion of the amidine (0.05 g, 0.25 mmol) was added and the mixture heated for 2.5 h. The pale yellow solution was allowed to cool then filtered and diluted with methanol (20 $cm^3$) before cooling at 5 °C overnight. The resulting pale yellow precipitate was recrystallised from dichloromethane–methanol to afford pale yellow microcrystals which were filtered off, washed with methanol followed by light petroleum (b.p. 60–80 °C) and dried *in vacuo*. Yield 0.07 g, 51%.

*Carbonyl*(N,N'-*diphenylbenzamidinato*)*hydridobis*(*triphenylphosphine*)*ruthenium*(II). Carbonyldihydridotris(triphenylphosphine)ruthenium (0.3 g, 0.34 mmol) was added to a stirred solution of *N,N'*-diphenylbenzamidine (0.50 g, 1.83 mmol) in toluene (12 $cm^3$) and the mixture heated under reflux for 6 h. The green solution was allowed to cool, filtered and diluted with

* *Supplementary data available* (No. SUP 56958, 4 pp.): $^{13}$C NMR data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

yellow crystals which formed were filtered off, washed with methanol followed by light petroleum and dried *in vacuo*. Yield 0.28 g, 88%.

The following analogues were similarly prepared as pale yellow crystals: *N,N'*-diphenylacetamidinato, 75% and *N,N'*-diphenylpropionamidinato 74%.

*Reactions involving* $[RuH(Cl)(CO)(PPh_3)_3]$.—*Carbonylchloro*(N,N'*-diphenylformamidinato)bis(triphenylphosphine)ruthenium*(II). Powdered $[RuH(Cl)(CO)(PPh_3)_3]$ (0.40 g, 0.42 mmol) was added to a stirred solution of *N,N'*-diphenylformamidine (0.33 g, 1.68 mmol) in toluene (20 $cm^3$) and the mixture heated under reflux for 4 h then allowed to cool and filtered. The filtrate was diluted with methanol (20 $cm^3$) and stirred overnight at 5 °C. The resulting yellow microcrystals were filtered off, washed with methanol followed by light petroleum and dried *in vacuo*. Yield 0.29 g, 81%.

The following analogues were similarly prepared: *N,N'*-diphenylbenzamidinato, yellow-green microcrystals (88%); *N,N'*-diphenylacetamidinato, yellow crystals (47%); and *N,N'*-diphenylpropionamidinato, yellow crystalline plates (50%).

*Carbonyl*(N,N'*-diphenylformamidinato)hydridobis(triphenylphosphine)ruthenium*(II). *N,N'*-Diphenylformamidine (0.30 g, 1.5 mmol) in ethanol (10 $cm^3$) and triethylamine (2 g, 20 mmol) were added to a solution of $[RuH(Cl)(CO)(PPh_3)_3]$ (0.30 g, 0.3 mmol) in benzene (12 $cm^3$) and the mixture heated under reflux for 2 h. After cooling the solution was filtered and diluted with methanol (25 $cm^3$) then left overnight at 5 °C. The resulting yellow microcrystals were filtered off, washed successively with methanol, water, methanol, and light petroleum, then dried *in vacuo*. Yield 0.19 g, 76%.

The following analogues were similarly prepared as yellow microcrystals: *N,N'*-diphenylbenzamidinato, 92%; *N,N'*-diphenylacetamidinato, 77%; and *N,N'*-diphenylpropionamidinato, 83%.

*Reactions involving* $[Ru(CO)_3(PPh_3)_2]$.—*Carbonyl*(N,N'*-diphenylformamidinato)hydridobis(triphenylphosphine)ruthenium*(II). Powdered $[Ru(CO)_3(PPh_3)_2]$ (0.30 g, 0.42 mmol) was added to a stirred solution of *N,N'*-diphenylformamidine (0.30 g, 1.5 mmol) in 2-methoxyethanol (10 $cm^3$) and the mixture heated under reflux for 4 h. The yellow solution was allowed to cool, filtered and diluted with methanol (30 $cm^3$) then set aside overnight at 5 °C. The resulting yellow crystals were filtered off, washed with methanol and light petroleum then dried *in vacuo*. Yield 0.22 g, 62%.

The following analogues were similarly prepared using a reaction time of 6 h: *N,N'*-diphenylbenzamidinato as yellow microcrystals (32%) and *N,N'*-diphenylacetamidinato, as pale yellow crystals (55%).

*Reactions involving* $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.75MeOH$.—*Carbonyl*(N,N'*-diphenylformamidinato)trifluoroacetatobis(triphenylphosphine)ruthenium*(II). Powdered $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.75MeOH$ (0.40 g, 0.45 mmol) was added to a stirred solution of *N,N'*-diphenylformamidine (0.08 g, 0.45 mmol) in benzene (20 $cm^3$) and the mixture heated under reflux for 30 min. Cooling, filtration and evaporation to dryness under reduced pressure gave a yellow solid which was crystallised from dichloromethane–methanol. The resulting yellow microcrystals were filtered off and washed successively with methanol, water, methanol and light petroleum then dried *in vacuo*. Yield 0.078 g, 20%.

The following analogues were similarly prepared: (*N,N'*-diphenylbenzamidinato, as yellow microcrystals (23%); (*N,N'*-diphenylacetamidinato, as pale yellow microcrystals (20%); and *N,N'*-diphenylpropionamidinato, as a mixture of *cis* and *trans* isomers, deposited as a yellow powder (27%).

*Carbonyl*(N,N'*-diphenylformamidinato)hydridobis(triphenylphosphine)ruthenium*(II). Powdered $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.75MeOH$ (0.50 g, 0.57 mmol) was added to a stirred solution of *N,N'*-diphenylformamidine (0.45 g, 2.3 mmol) and triethylamine (3 g, 30 mmol) in toluene (40 $cm^3$), and the mixture heated under reflux. After 4 h further portions of triethylamine (2 g, 20 mmol) and formamidine (0.20 g, 1 mmol) were added and the mixture refluxed for 4 h. The solution was then cooled, filtered and evaporated under reduced pressure. The residual yellow oil was crystallised from dichloromethane–methanol to give a yellow powder which was washed with methanol, water, methanol and light petroleum then dried *in vacuo*. Yield 0.18 g. The infrared spectrum showed trifluoroacetate bands [ν(OCO) 1632 $cm^{-1}$]. A further 3 h reflux with formamidine-triethylamine followed by isolation and crystallisation as described above gave the required product as yellow microcrystals (0.13 g, 30%).

*Carbonylbis*(N,N'*-diphenylbenzamidinato)(triphenylphosphine)ruthenium*(II). Powdered $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.75MeOH$ (0.50 g, 0.57 mmol) was added to a stirred solution of *N,N'*-diphenylbenzamidine (0.62 g, 2.27 mmol) and triethylamine (3 g, 30 mmol) in toluene (40 $cm^3$) and the mixture heated under reflux for 1.5 h. Additional triethylamine (1 g, 10 mmol) was then added. After heating for 1.5 h the solution was filtered, cooled and evaporated to dryness under reduced pressure. Crystallisation of the residue from dichloromethane–methanol followed by filtration and washing with methanol, water, methanol and light petroleum and drying *in vacuo* gave pale green microcrystals (0.22 g, 47%).

The following analogues were similarly prepared using a reaction time of 24 h: *N,N'*-diphenylacetamidinato, as yellow microcrystals (34%) and *N,N'*-diphenylpropionamidinato, as pale yellow microcrystals (27%).

*Reactions involving* $[RuH_2(PPh_3)_4]$.—*Carbonyl*(N,N'*-diphenylformamidinato)hydridobis(triphenylphosphine)ruthenium* (II). A mixture of $[RuH_2(PPh_3)_4]$ (0.5 g, 0.43 mmol) and *N,N'*-diphenylformamidine (0.84 g, 4.28 mmol) in 2-methoxyethanol (10 $cm^3$) was heated under reflux for 30 min. After cooling, yellow crystals were filtered off from the dark solution, washed with methanol and light petroleum, and dried *in vacuo*. Yield 0.26 g, 76%.

The following analogues were similarly prepared using a reaction time of 10 min: *N,N'*-diphenylbenzamidinato, as yellow crystals (62%); *N,N'*-diphenylacetamidinato, as yellow-brown microcrystals (54%); and *N,N'*-diphenylpropionamidinato, as yellow-brown microcrystals (76%).

'*Bis*(N,N'*-diphenylacetamidinato)bis(triphenylphosphine)ruthenium*(II)'. A mixture of $[RuH_2(PPh_3)_4]$ (0.40 g, 0.34 mmol) and *N,N'*-diphenylacetamidine (0.28 g, 1.34 mmol) in toluene (20 $cm^3$) was heated under reflux for 4 h. The dark suspension was allowed to cool and filtered to afford an orange powder which was washed successively with toluene, methanol and light petroleum and then dried *in vacuo*. Yield 0.14 g, 39%.

*Attempted synthesis of bis*(N,N'*-diphenylformamidinato)bis(triphenylphosphine)ruthenium*(II). A mixture of $[RuH_2(PPh_3)_4]$ (0.50 g, 0.43 mmol) and *N,N'*-diphenylformamidine (0.84 g, 4.4 mmol) in toluene (10 $cm^3$) was heated under reflux for 4 h. After cooling and filtering followed by evaporation of the filtrate under reduced pressure the residue was crystallised from dichloromethane–diethyl ether as a pale yellow solid. This was identified by spectroscopic methods as $[RuH\{PhNC(H)NPh\}(CO)(PPh_3)_2]$ (0.06 g, 16%). Attempts to prepare the complexes $[Ru\{PhNC(R)NPh\}_2(PPh_3)_2]$ (R = Ph or Et) under similar conditions afforded the corresponding hydrido carbonyl species $[RuH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ as yellow microcrystals identical with authentic samples.

*Reactions involving* $[RuCl_2(PPh_3)_3]$.—*Carbonyl*(N,N'*-diphenylformamidinato)hydridobis(triphenylphosphine)ruthenium*(II). A mixture of $[RuCl_2(PPh_3)_3]$ (0.30 g, 0.31 mmol), *N,N'*-diphenylformamidine (0.24 g, 1.22 mmol) and triethylamine (2 g, 20 mmol) in ethanol (20 $cm^3$) was heated under reflux for 4 h. Further portions (1 g) of triethylamine were added at hourly intervals. After cooling, the mixture was filtered then concentrated under reduced pressure to yield a yellow solid which was filtered off, washed with methanol, water, methanol and light petroleum then dried *in vacuo*. Yield 0.23 g, 87%.

The following analogues were similarly prepared as yellow microcrystals: *N,N'*-diphenylbenzamidinato, 57%; *N,N'*-diphenylacetamidinato, 93%; and *N,N'*-diphenylpropionamidinato, 73%.

*Carbonylchloro*(N,N'*-diphenylformamidinato)bis(triphenylphosphine)ruthenium*(II). Powdered $[RuCl_2(PPh_3)_3]$ (0.50 g, 0.5 mmol) was added to a stirred solution of *N,N'*-diphenylformamidine (0.4 g, 2 mmol) and triethylamine (1 g, 10 mmol) in toluene (20 $cm^3$) and the mixture heated under reflux for 3.5 h. Additional portions (1 g) of triethylamine were added after 70 and 140 min. After cooling, the mixture was filtered to afford dark green crystals. These were washed successively with methanol, water, methanol and light petroleum then dried *in vacuo*. Yield 0.15 g, 36%.

The diphenylacetamidinato analogue was similarly prepared in 93% yield. Attempts to prepare the corresponding propionamidinato and benzamidinato complexes under similar conditions gave $[RuH\{PhNC(Et)NPh\}(CO)(PPh_3)_2]$ and the mixture $[RuH\{PhNC(Ph)NPh\}(CO)(PPh_3)_2]$–$[RuCl\{PhNC(Ph)NPh\}(CO)(PPh_3)_2$ respectively after crystallisation from dichloromethane–methanol.

*Reactions involving* $[OsH_2(CO)(PPh_3)_3]$.—*Carbonyl*(N,N'*-diphenylbenzamidinato)hydridobis(triphenylphosphine)osmium*(II). A mixture of $[OsH_2(CO)(PPh_3)_3]$ (0.05 g, 0.05 mmol) and *N,N'*-diphenylbenzamidine (0.07 g, 0.25 mmol) in 2-methoxyethanol (25 $cm^3$) was heated under reflux for 24 h. After cooling, the mixture was taken to dryness under reduced pressure and the residual oily solid was crystallised from dichloromethane–methanol to give a yellow powder. This was filtered off, washed with methanol then light petroleum and dried *in vacuo*. Yield 0.02 g, 46%.

*Reactions involving* $[OsH(Cl)(CO)(PPh_3)_3]$.—*Carbonylchloro*(N,N'*-diphenylformamidinato)bis(triphenylphosphine)osmium*(II). A mixture of $[OsH(Cl)(CO)(PPh_3)_3]$ (0.48 g, 0.46 mmol) and *N,N'*-diphenylformamidine (0.75 g, 3.82 mmol) in toluene (15 $cm^3$) was heated under reflux for 6.5 h. The solution was then cooled, filtered, diluted with methanol (15 $cm^3$) and left overnight at 5 °C. The pale green microcrystals which deposited were filtered off, washed with methanol and light petroleum then dried *in vacuo*. Yield 0.24 g, 65%.

The following analogues were similarly prepared as yellow microcrystals using a reaction time of 24 h: *N,N'*-diphenylbenzamidinato, 33%, and *N,N'*-diphenylpropionamidinato, 33%.

*Reactions involving* $[Os(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.33MeOH$.—*Carbonyl*(N,N'*-diphenylformamidinato)trifluoroacetatobis(triphenylphosphine)osmium*(II). A mixture of $[Os(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.33MeOH$ (0.40 g, 0.41 mmol) and *N,N'*-diphenylformamidine (0.24 g, 1.2 mmol) in benzene (25 $cm^3$) was heated under reflux for 1.5 h. After cooling and evaporation under reduced pressure the yellow residue was crystallised from dichloromethane–methanol to give yellow platelets (0.13 g, 30%).

The following analogues were similarly prepared using a reaction time of 2 h: *N,N'*-diphenylbenzamidinato, as yellow microcrystals (39%); *N,N'*-diphenylacetamidinato, as yellow platelets (50%); and *N,N'*-diphenylpropionamidinato, as pale yellow microcrystals (56%).

*Carbonyl*(N,N'*-diphenylformamidinato)hydridobis(triphenylphosphine)osmium*(II). A mixture of $[Os(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.33MeOH$ (0.40 g, 0.41 mmol), *N,N'*-diphenylformamidine (0.15 g, 0.8 mmol) and triethylamine (3 g, 30 mmol) in toluene (25 $cm^3$) was heated under reflux for 2 h. The mixture was then treated with additional triethylamine (1 g) and refluxed for 4 h. Cooling, filtering and evaporation under reduced pressure gave a yellow-orange solid. This was crystallised from dichloromethane–methanol to give yellow microcrystals which were filtered off, successively washed with methanol, water, methanol and light petroleum then dried *in vacuo*. Yield 0.06 g, 32%.

The following analogues were similarly prepared: *N,N'*-diphenylbenzamidinato, as yellow microcrystals (43%); *N,N'*-diphenylacetamidinato, after a total reaction time of 15 h, as yellow-brown microcrystals (23%); and *N,N'*-diphenylpropionamidinato, as yellow-brown microcrystals (21%).

*Reactions involving* $[OsH_4(PPh_3)_3]$.—*Carbonyl*(N,N'*-diphenylformamidinato)hydridobis(triphenylphosphine)osmium*(II). A mixture of $[OsH_4(PPh_3)_3]$ (0.10 g, 0.1 mmol) and *N,N'*-diphenylformamidine (0.20 g, 1 mmol) in 2-methoxyethanol (5 $cm^3$) was heated under reflux for 2 h. After cooling the mixture, yellow microcrystals were filtered off, washed successively with methanol and light petroleum then dried *in vacuo*. Yield 0.04 g, 42%.

The *N,N'*-diphenylbenzamidinato analogue was similarly prepared using a reaction time of 4 h, and was isolated by evaporation of the filtered reaction solution to dryness under reduced pressure. The crude product was crystallised from dichloromethane–methanol and the yellow microcrystals washed and dried as above. Yield 56%.

*Carbonyl*(N,N'*-diphenylacetamidinato)hydridobis(triphenylphosphine)osmium*(II). A mixture of $[OsH_4(PPh_3)_3]$ (0.40 g, 0.4 mmol) and *N,N'*-diphenylacetamidine (0.85 g, 4 mmol) in 2-methoxyethanol (25 $cm^3$) was heated under reflux for 4 h then cooled, diluted with methanol (20 $cm^3$) and left overnight at 5 °C. A mixture of product and starting materials which deposited was filtered off, and added to a solution of *N,N'*-diphenylacetamidine (0.45 g, 2.1 mmol) in 2-methoxyethanol (20 $cm^3$). The mixture was heated under reflux for 24 h, cooled, filtered and evaporated to dryness under reduced pressure. The residue was crystallised from dichloromethane–methanol as pale yellow needles. These were filtered off, washed with methanol and light petroleum then dried *in vacuo*. Yield 0.10 g, 26%. The *N,N'*-diphenylpropionamidinato analogue was similarly prepared as pale yellow microcrystals (31%).

*Reaction involving* $[OsCl_2(PPh_3)_3]$.—*Carbonyl*(N,N'*-diphenylbenzamidinato)hydridobis(triphenylphosphine)osmium*(II). A mixture of $[OsCl_2(PPh_3)_3]$ (0.3 g, 0.29 mmol), *N,N'*-diphenylbenzamidine (0.31 g, 1.14 mmol) and triethylamine (1 g) in toluene (20 $cm^3$) was heated under reflux for 4 h. During reflux further portions (1 g) of triethylamine were added at intervals of 1 h. After cooling, the solution was filtered and then evaporated to dryness under reduced pressure. Crystallisation of the residue from dichloromethane–methanol gave yellow microcrystals (0.10 g, 34%).

*Reactions involving* $[IrHCl_2(PPh_3)_3]$.—*Chloro*(N,N'*-diphenylformamidinato)hydridobis(triphenylphosphine)iridium*(III). A mixture of $[IrHCl_2(PPh_3)_3]$ (0.30 g, 0.28 mmol), *N,N'*-diphenylformamidine (0.22 g, 1.10 mmol) and triethylamine (3 g, 30 mmol) in benzene (25 $cm^3$) was heated under reflux for 3 h. A further portion of triethylamine (1 g) was added after 1.5 h of reflux. The dark yellow reaction solution was allowed to cool, filtered and then evaporated to dryness under reduced pressure. The residual solid was crystallised from dichloromethane–methanol to give yellow microcrystals. These were filtered off, washed successively with methanol, water, methanol and light petroleum then dried *in vacuo*. Yield 0.12 g, 45%.

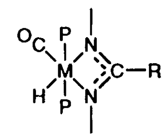
The following analogues were similarly prepared as yellow microcrystals: *N,N'*-diphenylbenzamidinato, 56%; *N,N'*-diphenylacetamidinato, 60%; and *N,N'*-diphenylpropionamidinato, 52%.

*Dichloro*(N,N'*-diphenylbenzamidinato)bis(triphenylphosphine)iridium*(III). A mixture of $[IrHCl_2(PPh_3)_3]$ (0.40 g, 0.38

mmol) and *N,N'*-diphenylbenzamidine (0.31 g, 1.14 mmol) in toluene (60 $cm^3$) was heated under reflux for 24 h. The mixture was cooled, filtered to remove a trace of brown powder (0.04 g). The filtrate was taken to dryness under reduced pressure and the residual solid crystallised from dichloromethane–methanol to afford yellow microcrystals. These were washed with methanol and light petroleum then dried *in vacuo*. Yield 0.12 g, 29%.

*Reactions involving mer*-$[IrH_3(PPh_3)_3]$.—(*N,N'-Diphenylformamidinato*)*dihydridobis*(*triphenylphosphine*)*iridium*(III). A mixture of *mer*-$[IrH_3(PPh_3)_3]$ (0.30 g, 0.30 mmol) and *N,N'*-diphenylformamidine (0.24 g, 1.2 mmol) in toluene (25 $cm^3$) was heated under reflux for 8 h. The dark yellow solution was allowed to cool, filtered and then evaporated to dryness under reduced pressure. The residual yellow solid was crystallised from dichloromethane–methanol to afford yellow microcrystals (0.08 g, 29%).

The *N,N'*-diphenylbenzamidinato analogue was similarly prepared as yellow microcrystals (37%). Similar reactions involving *N,N'*-diphenyl-acetamidine and -propionamidine gave mixtures of product and unreacted *mer*-$[IrH_3(PPh_3)_3]$ even after 24 h reflux.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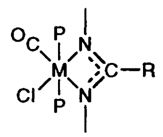
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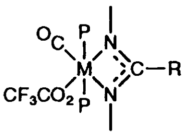
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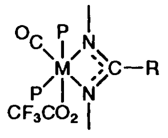
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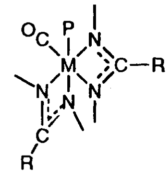
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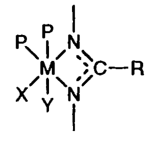
**VIa** X = CO, Y = Cl
**VIb** X = Cl, Y = CO

## Results and Discussion

*General.*—This work is concerned with the reactions of four *N,N'*-diphenylamidines PhNC(R)NHPh, namely *N,N'*-diphenyl-formamidine (R = H), -acetamidine (R = Me), propionamidine (R = Et) and -benzamidine (R = Ph), with an extensive range of phosphine-containing ruthenium, osmium and iridium complexes. The reactivity of the chosen amidines towards these precursors shows a significant dependence upon the nature of the substituent R, and generally decreases in the order H > Ph > Me ≈ Et. This sequence parallels the decreasing acidity (increasing $pK_a$ values) of the corresponding carboxylic acids $RCO_2H$, and thus suggests that ease of deprotonation of the amidines is a rate-determining factor in these reactions. The reactions between amidines and platinum-metal precursors examined in this study generally afford products analogous to those obtained under similar conditions with 1,3-diaryltriazenes[2–4] and various carboxylic acids.[13,14] However, they differ in one important respect. Reactions of amidines with the carbonyl-free precursors $[RuH_2(PPh_3)_4]$, $[OsH_4(PPh_3)_3]$ and $[MCl_2(PPh_3)_3]$ (M = Ru or Os) are accompanied by an avid carbonyl-abstraction reaction if traces of alcohol are present. This behaviour, which has no parallel with triazenes or carboxylic acids, even when neat alcohol is employed as reaction medium, leads to isolation of carbonyl-contaning amidinato complexes in good yield.

All the products isolated in this work are stable in the open laboratory for periods of several months. The *N,N'*-diphenylformamidinato products have physical and spectroscopic properties very similar to those previously reported for the *N,N'*-di-*p*-tolylformamidinato complexes obtained by insertion of *N,N'*-di-*p*-tolylcarbodiimide into metal–hydride bonds.[6,7] In particular the central proton of the co-ordinated formamidinate ligand PhNC(*H*)NPh resonates at low field (δ *ca.* 8) thus suggesting significant electron delocalisation within the amidinato chelate ring.

*Reactions involving* $[RuH_2(CO)(PPh_3)_3]$.—*N,N'*-Diphenylamidines PhNC(R)NHPh (R = H, Me, Et or Ph) react with $[RuH_2(CO)(PPh_3)_3]$ in boiling benzene–ethanol or toluene over a period of 2–6 h to yield yellow or green solutions from which yellow crystals of the products [RuH{PhNC(R)NPh}-$(CO)(PPh_3)_2]$ can be isolated in good yield. Spectroscopic data (Tables 2–4) are indicative of the *trans*-phosphine stereochemistry **I**, (M = Ru). In the formamidinato complex coupling of the central proton NC(*H*)N to the two phosphorus nuclei is observed (triplet, $^4J_{HP}$ 2 Hz) and in the acetamidinato complex a small coupling of the methyl protons $NC(CH_3)N$ to the phosphorus nuclei is resolved (triplet, $^5J_{HP}$ 1.5 Hz).

*Reactions involving* $[RuH(Cl)(CO)(PPh_3)_3]$.—Reactions of *N,N'*-diphenylamidines with $[RuH(Cl)(CO)(PPh_3)_3]$ and an excess of triethylamine in benzene–ethanol afford excellent yields of the hydrido complexes [RuH{PhNC(R)NPh}(CO)-$(PPh_3)_2]$ identical with those described above. When the amidines react with $[RuH(Cl)(CO)(PPh_3)_3]$ in boiling toluene over a period of *ca.* 4 h yellow crystals of the chloro complexes [RuCl{PhNC(R)NPh}(CO)$(PPh_3)_2]$ are obtained. Spectroscopic data for these products (Tables 2 and 3) are consistent with the *trans* phosphine stereochemistry **II** (M = Ru). Confirmation of this assignment is provided by the $^{13}C$-{$^1H$} NMR spectra (Table 4) which display a virtually coupled triplet for the carbons bonded to phosphorus in the triphenylphosphine ligands. Small couplings are also observed between the $^{31}P$ nuclei and the protons of the formamidinate ligands ($^4J_{HP}$ 2.5 Hz) and acetamidinate ligands ($^5J_{HP}$ 1.5 Hz). Phosphorus-31 decoupling confirms these assignments.

*Reactions involving* $[Ru(CO)_3(PPh_3)_2]$.—The hydrido complexes [RuH{PhNC(R)NPh}(CO)$(PPh_3)_2]$ have also been obtained in good yield from the reactions of *N,N'*-diphenylamidines with $[Ru(CO)_3(PPh_3)_2]$ in refluxing 2-methoxyethanol. These reactions presumably involve oxidative addition of the amidine N–H bond across the ruthenium(0) centre with concomitant elimination of a molecule of carbon monoxide to give the intermediate dicarbonyls [RuH{PhNC(R)NPh}$(CO)_2$-$(PPh_3)_2]$. Loss of a further molecule of CO and co-ordination of the second nitrogen of the amidinate ligand generates the final product.

*Reactions involving* $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$·0.75MeOH.—*N,N'*-Diphenylamidines react with $[Ru(O_2CCF_3)_2(CO)$-$(PPh_3)_2]$·0.75MeOH in boiling benzene over a period of *ca.* 30 min to afford the yellow crystalline trifluoroacetates [Ru-$(O_2CCF_3)${PhNC(R)NPh}(CO)$(PPh_3)_2]$ in modest yield. Two of these products (R = H or Me) gave NMR spectra ($^{31}P$-{$^1H$} singlet, $^{13}C$ virtually coupled triplet) indicative of the *trans*-phosphine stereochemistry **III** (M = Ru). A third (R = Ph) displayed a $^{31}P$-{$^1H$} NMR AX pattern which, given the tendency of CO ligands to bond *trans* to N rather than P, strongly suggests the *cis*-phosphine isomer **IV** (M = Ru). The

**Table 1** Melting point and analytical data (calculated values in parentheses)

| | | | Analysis (%) | | |
|---|---|---|---|---|---|
| Complex | R | M.p./°C | C | H | N |
| [RuH{PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | 218–222 | 70.20 (70.65) | 4.80 (5.00) | 3.25 (3.30) |
| | Ph | 208–211 | 72.00 (72.65) | 5.10 (5.00) | 3.20 (3.05) |
| | Me | 256–258 | 70.85 (70.90) | 5.00 (5.15) | 3.15 (3.25) |
| | Et | 202–205 | 70.85 (71.15) | 5.30 (5.30) | 3.20 (3.20) |
| [RuCl{PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | 286–288 | 67.75 (67.90) | 4.45 (4.65) | 3.15 (3.15) |
| | Ph | 256–259 | 69.50 (70.00) | 4.70 (4.70) | 2.90 (2.90) |
| | Me | 262–264 | 68.40 (68.20) | 4.70 (4.80) | 3.15 (3.10) |
| | Et | 213–216 | 69.25 (68.45) | 4.95 (4.95) | 2.70 (3.05) |
| [Ru($O_2CCF_3$){PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | 262–264 | 64.70 (64.95) | 4.10 (4.30) | 2.90 (2.90) |
| | Ph | 199–202 | 66.65 (67.10) | 4.30 (4.35) | 2.60 (2.70) |
| | Me | 237–239 | 65.15 (65.25) | 4.05 (4.45) | 2.95 (2.85) |
| | Et | — | 64.65 (65.50) | 4.45 (4.60) | 2.65 (2.85) |
| [Ru{PhNC(R)NPh}$_2$(CO)($PPh_3$)] | Ph | 222–224 | 73.30 (73.30) | 4.75 (4.85) | 6.00 (6.00) |
| | Me | 215–216 | 69.45 (69.70) | 4.95 (5.10) | 6.85 (6.90) |
| | Et | 153–158 | 70.05 (70.25) | 5.10 (5.40) | 6.65 (6.70) |
| [Ru{PhNC(R)NPh}$_2$($PPh_3$)$_2$] | Me | 268–271 | 73.25 (73.60) | 5.20 (5.40) | 5.30 (5.35) |
| [OsH{PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | — | 63.65 (63.95) | 4.45 (4.50) | 3.00 (3.00) |
| | Ph[a] | 231–233 | 64.45 (64.15) | 4.45 (4.50) | 2.50 (2.65) |
| | Me[a] | 252–254 | 62.40 (62.15) | 4.15 (4.65) | 2.65 (2.80) |
| | Et | 221–223 | 64.15 (64.60) | 4.65 (4.80) | 2.75 (2.90) |
| [OsCl{PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | 279–281 | 61.50 (61.70) | 4.10 (4.25) | 2.85 (2.90) |
| | Ph | 248–250 | 64.70 (64.10) | 4.35 (4.30) | 2.45 (2.65) |
| | Et | — | 62.50 (62.35) | 4.35 (4.55) | 2.75 (2.80) |
| [Os($O_2CCF_3$){PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | 212–213 | 59.30 (59.40) | 3.70 (3.95) | 2.85 (2.65) |
| | Ph | 279–281 | 62.05 (61.80) | 3.75 (4.00) | 2.40 (2.50) |
| | Me[b] | 235–239 | 56.85 (59.75) | 3.75 (4.05) | 2.45 (2.65) |
| | Et | 254–257 | 59.25 (60.10) | 3.70 (4.20) | 2.55 (2.60) |
| [IrH(Cl){PhNC(R)NPh}($PPh_3$)$_2$] | H | 229–230 | 61.80 (62.05) | 4.40 (4.45) | 2.70 (2.95) |
| | Ph | 225–226 | 64.00 (64.50) | 4.35 (4.55) | 2.65 (2.75) |
| | Me | 215–218 | 60.00 (60.35) | 4.35 (4.50) | 2.70 (2.80) |
| | Et | 210–212 | 60.75 (60.70) | 4.50 (4.65) | 2.65 (2.75) |
| [$IrCl_2${PhNC(R)NPh}($PPh_3$)$_2$] | Ph[b] | 249–251 | 58.75 (62.40) | 4.90 (4.30) | 2.40 (2.65) |
| [$IrH_2${PhNC(R)NPh}($PPh_3$)$_2$] | H | 250–253[c] | 63.35 (64.40) | 4.30 (4.75) | 2.50 (3.05) |
| | Ph | 240–244[c] | 66.15 (66.70) | 4.65 (4.80) | 2.60 (2.85) |

[a] Analysis figures include 0.5 mol $CH_2Cl_2$. [b] Gave good spectroscopic data but consistently low carbon analysis. [c] Decomposition.

fourth product (R = Et) had a $^{31}P-\{^1H\}$ NMR spectrum consistent with a mixture of *trans*- and *cis*-phosphine isomers **III** and **IV**.

Similar reactions performed in boiling toluene in the presence of an excess of triethylamine afford the hydrido carbonyl [RuH{PhNC(H)NPh}(CO)($PPh_3$)$_2$] **I** (M = Ru) or the bis-(amidinato) products [Ru{PhNC(R)NPh}$_2$(CO)($PPh_3$)] (R = Me, Et, or Ph). The latter complexes show $^1H$ NMR spectra indicative of the *cis* stereochemistry **V**. Thus the acetamidinato derivative (R = Me) generates two methyl resonances (relative intensities 1 : 1) and the propionamidinato derivative generates two ethyl patterns each displaying diastereotopic $CH_2$ groups.

*Reactions involving* [$RuH_2$($PPh_3$)$_4$].—The reactions of *N,N'*-diphenylamidines with [$RuH_2$($PPh_3$)$_4$] in boiling 2-methoxyethanol are accompanied by a carbonyl-abstraction process leading to formation of the hydridocarbonyl products [RuH{PhNC(R)NPh}(CO)($PPh_3$)$_2$] in good yield. These reactions are in sharp contrast to corresponding ones involving 1,3-diaryltriazenes and carboxylic acids which yield the non-carbonylated products [Ru(PhNNNPh)$_2$($PPh_3$)$_2$][3] and [RuH($O_2CR$)($PPh_3$)$_3$][13,14] respectively under similar conditions. In an attempt to prepare non-carbonylated amidinato complexes the above reactions were repeated using toluene as solvent. With *N,N'*-diphenylacetamidine a product analysing as [Ru{PhNC(Me)NPh}$_2$($PPh_3$)$_2$] precipitated in fair yield as an orange powder. However it was too insoluble for solution spectroscopic studies and its true identity is uncertain (see below). The other amidines employed gave poor yields of the hydrido carbonyls [RuH{PhNC(R)NPh}(CO)($PPh_3$)$_2$] even when toluene freshly distilled from sodium was employed as solvent. We suggest (see below) that the formation of the hydridocarbonyls involves abstraction of CO from traces of alcohol associated with the [$RuH_2$($PPh_3$)$_4$] and demonstrates the avidity of the carbonyl-abstraction reaction. Deliberate addition of small amounts of alcohol lead to a much enhanced yield of the hydridocarbonyl products.

*Reactions involving* [$RuCl_2$($PPh_3$)$_3$].—Avid carbonyl abstraction is also a feature of reactions between [$RuCl_2$($PPh_3$)$_3$] and *N,N'*-diphenylamidines in alcoholic and 'non-alcoholic' media. Thus refluxing a mixture of these reagents with an excess of triethylamine in ethanol for *ca.* 4 h affords the ubiquitous products [RuH{PhNC(R)NPh}(CO)($PPh_3$)$_2$] in good yield. When the same reactions are performed in refluxing toluene the products obtained are the chlorocarbonyls [RuCl{PhNC(R)NPh}(CO)($PPh_3$)$_2$] (R = H or Me), the hydridocarbonyl [RuH{PhNC(R)NPh}(CO)($PPh_3$)$_2$] (R = Et) or a mixture of the two (R = Ph). Again formation of carbonyl products from reactions conducted in 'alcohol free' media attests to the high carbonyl-abstracting power of these ruthenium-amidine systems.

*Reactions involving* [$OsH_2$(CO)($PPh_3$)$_3$].—The osmium dihydride [$OsH_2$(CO)($PPh_3$)$_3$], unlike its ruthenium analogue, reacted only very slowly with *N,N'*-diphenylamidines. Thus even with one of the more reactive amidines PhNC(Ph)NHPh the expected product [OsH{PhNC(Ph)NPh}(CO)($PPh_3$)$_2$] was still contaminated with [$OsH_2$(CO)($PPh_3$)$_3$] after heating the mixture in boiling 2-methoxyethanol for a period in excess of 24 h. Therefore, since products of this type are more readily

Table 2 Infrared spectroscopic data ($cm^{-1}$)

| Complex | R | ν(M–H) | ν(C=O) | ν(N–C–N) | ν(M–Cl) |
|---|---|---|---|---|---|
| $[RuH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | 2037 | 1900 | 1593 | — |
| | Ph | — | 1921 | 1589 | — |
| | Me | 2043 | 1921 | 1591 | — |
| | Et | 2046 | 1919 | 1589 | — |
| $[RuCl\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | — | 1920 | 1592 | 306 |
| | Ph | — | 1916 | 1590 | 304 |
| | Me | — | 1934 | 1590 | 304 |
| | Et | — | 1922 | 1590 | 294 |
| $[Ru(O_2CCF_3)\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | — | 1932 | 1593 | — |
| | Ph | — | 1957 | 1592 | — |
| | Me | — | 1941 | 1591 | — |
| | Et | — | 1968, 1955 | 1592 | — |
| $[Ru\{PhNC(R)NPh\}_2(CO)(PPh_3)]$ | Ph | — | 1929 | 1591 | — |
| | Me | — | 1930 | 1589 | — |
| | Et | — | 1917 | 1590 | — |
| $[Ru\{PhNC(R)NPh\}_2(PPh_3)_2]$ | Me | — | — | 1593 | — |
| $[OsH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | 2130 | 1881 | 1594 | — |
| | Ph | 2027 | 1886 | 1591 | — |
| | Me | 2136 | 1903 | 1590 | — |
| | Et | 2057 | 1903 | 1588 | — |
| $[OsCl\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | — | 1908 | 1596 | 297 |
| | Ph | — | 1896 | 1592 | 299 |
| | Me | — | 1908 | 1590 | 298 |
| | Et | — | 1918 [1896(sh)] | 1590 | 272 |
| $[Os(O_2CCF_3)\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | — | 1947 | 1596 | — |
| | Ph | — | 1941 | 1594 | — |
| | Me | — | 1951 | 1594 | — |
| | Et | — | 1951 | 1593 | — |
| $[IrH(Cl)\{PhNC(R)NPh\}(PPh_3)_2]$ | H | 2201 | — | 1597 | 306 |
| | Ph | 2180 | — | 1593 | 298 |
| | Me | 2267 | — | 1592 | 303 |
| | Et | 2269 | — | 1592 | 301 |
| $[IrCl_2\{PhNC(R)NPh\}(PPh_3)_2]$ | Ph | — | — | 1592 | 303 |
| $[IrH_2\{PhNC(R)NPh\}(PPh_3)_2]$ | H | 2180, 2160 | | 1595 | — |
| | Ph | 2187, 2159 | | 1590 | — |
| | Me* | 2137(br) | | 1592 | — |
| | Et* | 2074(br) | | 1597 | — |

[a] As impure samples containing $[IrH_3(PPh_3)_3]$, ν(Ir–H) 1745 $cm^{-1}$.

obtained from $[OsH_4(PPh_3)_3]$, further reactions involving $[OsH_2(CO)(PPh_3)_3]$ were not pursued.

*Reactions involving* $[OsH(Cl)(CO)(PPh_3)_3]$.—Reactions between *N,N'*-diphenylamidines and $[OsH(Cl)(CO)(PPh_3)_3]$ in boiling toluene gave the expected products $[OsCl\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ in fair yield. However, with the exception of the most reactive amidine PhNC(H)NHPh, reaction times of 24 h were required and even then reaction was incomplete in one instance (R = Me). Like their ruthenium analogues these products show $^{31}P$ and $^{13}C$ NMR spectra indicative of stereochemistry **II** (M = Os). Additional $^{31}P$ resonances (AX pattern) in the spectrum of the propionamidinato derivative are attributed to the presence of a second (*cis*-phosphine) isomer. Since phosphine is more likely to be *trans* to chloride than carbonyl stereochemistry **VIa** (M = Os) is preferred over **VIb** (M = Os).

*Reactions involving* $[Os(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.33MeOH$.—Heating $[Os(O_2CCF_3)_2(CO)(PPh_3)_2]\cdot0.33MeOH$ with *N,N'*-diphenylamidines in benzene for *ca.* 1.5–2 h affords the products $[Os(O_2CCF_3)\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ in modest yield. In contrast to their ruthenium analogues these osmium species display $^{31}P$ NMR spectra (AX patterns) indicative of a *cis*-phosphine stereochemistry, probably with trifluoroacetate rather than carbonyl *trans* to phosphine. The proton spectrum of the formamidinato derivative shows couplings of the NC(*H*)N proton to *cis*- and *trans*-phosphines [$^4J_{HP}$ 1.5 (*cis*), 6 Hz (*trans*)]. When the same reagents are heated under reflux with an excess of triethylamine in toluene the hydridocarbonyl products are obtained in fair yield.

*Reactions involving* $[OsH_4(PPh_3)_3]$.—Reactions between *N,N'*-diphenylamidines and $[OsH_4(PPh_3)_3]$ in boiling 2-methoxyethanol are accompanied by a carbonyl-abstraction reaction, similar to that encountered with $[RuH_2(PPh_3)_4]$, and afford hydridocarbonyls $[OsH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ in modest yield. Once more the behaviour of the diphenylamidines contrasts sharply with that of the corresponding triazene which under the same conditions generates the carbonyl-free complex $[OsH_3(PhNNNPh)(PPh_3)_2]$ in good yield.[3]

*Reaction involving* $[OsCl_2(PPh_3)_3]$.—The hydridocarbonyl $[OsH\{PhNC(Ph)NPh\}(CO)(PPh_3)_2]$ is also obtained in modest yield when a mixture of $[OsCl_2(PPh_3)_3]$, *N,N*-diphenylbenzamidine and triethylamine is heated under reflux in toluene for 4 h.

*Reactions involving mer*-$[IrH_3(PPh_3)_3]$.—*N,N'*-Diphenylamidines PhNC(R)NHPh (R = H or Ph) react with *mer*-$[IrH_3(PPh_3)_3]$ in boiling toluene over a period of 8 h to form the dihydrido species $[IrH_2\{PhNC(R)NPh\}(PPh_3)_2]$. The less-reactive amidines (R = Me or Et) gave mixtures of product and starting material even after 24 h reflux. The $^{31}P-\{^1H\}$ and $^1H$ NMR data (Table 3) are indicative of *trans*-phosphine stereochemistry.

**Table 3** Proton and $^{31}P-\{^1H\}$ NMR spectroscopic data[a]

| Complex | R | MH | CR | $PPh_3$ |
|---|---|---|---|---|
| $[RuH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | $-13.37$ (t, $^2J_{HP}$ 20) | 7.73 (t, $^4J_{HP}$ 2) | 48.93 (s) |
| | Ph | $-12.62$ (t, $^2J_{HP}$ 21) | — | 46.98 (s) |
| | Me | $-12.94$ (t, $^2J_{HP}$ 20) | 1.35 (t, $^5J_{HP}$ 1.5) | 47.92 (s) |
| | Et | $-12.89$ (t, $^2J_{HP}$ 21) | 0.5 (t), 1.78 (q), $^3J_{HH}$ 7.5 | 46.66 (s) |
| $[RuCl\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | | 7.90 (t, $^4J_{HP}$ 2.5) | 29.67(s) |
| | Ph | | — | 29.35 (s) |
| | Me | | 1.71 (t, $^5J_{HP}$ 1.5) | 29.46 (s) |
| | Et | | 0.81 (t), 2.16 (q), $^3J_{HH}$ 7.5 | 29.53 (s) |
| $[Ru(O_2CCF_3)\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | | Masked | 36.04 (s) |
| | Ph | | — | 47.93, 40.00 (AX, $^2J_{PP}$ 22.5) |
| | Me | | 1.27 (t, $^5J_{HP}$ 2.5) | 34.65 (s) |
| | Et[b] | | 0.52 (t), 1.68 (q), $^3J_{HH}$ 7.5 | 34.36 (s) |
| | Et[c] | | 0.63 (t), 1.92 (d of q), 2.31 (d of q), $^2J_{HH}$ 14, $^3J_{HH}$ 7.5 | 45.85, 41.24 (AX, $^2J_{PP}$ 25.5) |
| $[Ru\{PhNC(R)NPh\}_2(CO)(PPh_3)]$ | Ph | | — | 51.81 (s) |
| | Me | | 1.66 (s), 1.96 (s) | 53.21 (s) |
| | Et | | 0.37 (t), 0.64 (t), 2.40 (m) 2.20 (m, $^3J_{HH}$ 7.5) | 52.18 (s) |
| $[Ru\{PhNC(R)NPh\}_2(PPh_3)_2]$ | Me | | — | — |
| $[OsH\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | $-14.57$ (t of d, $^2J_{HP}$ 17, $^4J_{HH}$ 1) | 8.76 (t of d, $^4J_{HP}$ 2, $^4J_{HH}$ 1) | 21.81 (s) |
| | Ph | $-13.83$ (t, $^2J_{HP}$ 18.5) | | 20.13 (s) |
| | Me | $-14.28$ (t, $^2J_{HP}$ 17.5) | 1.41 (t, $^5J_{HP}$ 1.5) | 20.40 (s) |
| | Et | $-14.09$ (t, $^2J_{HP}$ 18) | 0.58 (t), 1.77 (q), $^3J_{HH}$ 7.5 | 19.37 (s) |
| $[OsCl\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | | 8.69 (t, $^4J_{HP}$ 2) | 0.57 (s) |
| | Ph | | — | $-0.58$ (s) |
| | Me | | 1.45 (s) | $-0.43$ (s) |
| | Et[b] | | 0.86 (t), 2.25 (q), $^3J_{HH}$ 7.5 | $-0.68$ (s) |
| | Et[c] | | 0.42 (t), 1.73 (d of q), 2.07 (d of q), $^2J_{HH}$ 14, $^3J_{HH}$ 7.5 | 4.06, 0.35 (AX, $^2J_{PP}$ 10.5) |
| $[Os(O_2CCF_3)\{PhNC(R)NPh\}(CO)(PPh_3)_2]$ | H | | 9.20 (d of d, $^4J_{HP}$ 6, 1.5) | 3.29, 1.24 (AX, $^2J_{PP}$ 10) |
| | Ph | | — | 3.98, $-0.04$ (AX, $^2J_{PP}$ 10) |
| | Me | | 1.66 (s) | 5.58, $-1.95$ (AX, $^2J_{PP}$ 10) |
| | Et | | 0.69 (t), 1.88 (d of q), 2.32 (d of q), $^2J_{HH}$ 15, $^3J_{HH}$ 7.5 | 5.56, $-3.17$ (AX, $^2J_{PP}$ 10) |
| $[IrH(Cl)\{PhNC(R)NPh\}(PPh_3)_2]$ | H | $-24.85$ (t, $^2J_{HP}$ 14) | 8.87 (t, $^4J_{HP}$ 2) | 6.16 (s) |
| | Ph | $-23.16$ (t, $^2J_{HP}$ 14.5) | — | 5.86 (s) |
| | Me | $-23.26$ (t, $^2J_{HP}$ 14) | 1.59 (t, $^5J_{HP}$ 1.5) | 4.11 (s) |
| | Et | $-23.31$ (t, $^2J_{HP}$ 14) | 0.62 (t), 1.82 (q), $^3J_{HH}$ 7.5 | 5.22 (s) |
| $[IrCl_2\{PhNC(R)NPh\}(PPh_3)_2]$ | Ph | | — | $-25.04$ (s) |
| $[IrH_2\{PhNC(R)NPh\}(PPh_3)_2]$ | H | $-22.82$ (t, $^2J_{HP}$ 16.5) | 9.15 (br) | 22.67 (s) |
| | Ph | $-22.85$ (t, $^2J_{HP}$ 17.5) | — | 20.33 (s) |
| | Me[d] | $-22.40$ (t, $^2J_{HP}$ 17) | 1.41 (s) | 22.18 (s) |
| | Et[d] | $-22.60$ (t, $^2J_{HP}$ 17.5) | 0.65 (t), 1.85 (q), $^3J_{HH}$ 7.5 | 20.17 (s) |

[a] d = Doublet, t = triplet, q = quartet, m = multiplet, br = broad unresolved resonance; *J* in Hz. [b] *trans*-Phosphine isomer. [c] *cis*-Phosphine isomer. [d] Impure sample.

*Reactions involving* $[IrHCl_2(PPh_3)_3]$.—Mixtures of $[IrHCl_2(PPh_3)_3]$, *N,N'*-diphenylamidines and an excess of triethylamine in boiling benzene afford the chlorohydrido complexes $[IrH(Cl)\{PhNC(R)NPh\}(PPh_3)_2]$ in good yield. The $^{31}P-\{^1H\}$ and high-field $^1H$ NMR spectra are indicative of *trans*-phosphine stereochemistry.

Attempts to form the corresponding dichloro complexes $[IrCl_2\{PhNC(R)NPh\}(PPh_3)_2]$ from amidines and $[IrHCl_2(PPh_3)_3]$ in boiling toluene gave a modest yield of the benzamidinato product $[IrCl_2\{PhNC(Ph)NPh\}(PPh_3)_2]$ but yielded only intractable mixtures with other amidines.

*The Carbonyl-abstraction Process*.—As noted above, reactions involving the carbonyl-free precursors $[RuCl_2(PPh_3)_3]$, $[RuH_2(PPh_3)_4]$, $[OsCl_2(PPh_3)_3]$ and $[OsH_4(PPh_3)_3]$ are accompanied by carbonyl formation if traces of alcohols or similar CO sources are present. This behaviour contrasts sharply with that previously observed for the closely related 1,3-diaryltriazenes (RNNNHR) and carboxylic acids ($RCO_2H$) which yield carbonyl-free products in good yield under similar conditions even when copious quantities of ethanol are present. Thus with $[RuH_2(PPh_3)_4]$ the products obtained are of the form $[Ru(RNNNR)_2(PPh_3)_2]$[3] and $[RuH(O_2CR)(PPh_3)_3]$[13,14] respectively. We believe that the disparate nature of these reaction products can be rationalised in terms of equations (1)–(4) in which all three ligand types (HL) generate an initial product of the form $[RuH(L)(PPh_3)_3]$.

$$[RuH_2(PPh_3)_4] + HL \longrightarrow [RuH(L)(PPh_3)_3] + H_2 + PPh_3 \quad (1)$$

$$[RuH(O_2CR)(PPh_3)_3] \xrightarrow{RCO_2H} \!\!\!\!\!\!\times \quad (2)$$

$$[RuH(RNNNR)(PPh_3)_3] \xrightarrow{RNNNHR} [Ru(RNNNR)_2(PPh_3)_2] + Hz + PPh_3 \quad (3)$$

$$[RuH\{PhNC(R)NPh\}(PPh_3)_3] \xrightarrow[\text{CO source}]{PhNC(R)NHPh} [RuH\{PhNC(R)NPh\}(CO)(PPh_3)_2] + PPh_3 \quad (4)$$

The carboxylates $[RuH(O_2CR)(PPh_3)_3]$ fail to react further because the relatively high acidity of the carboxylic acids and

**Table 4** Selected $^{13}C$ NMR data[a]

| | | | | δ(R) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Complex | R | δ(CO) | δ(NCN) | $C^1$ | $C^2$ | $C^3$ | $C^4$ | Me | $CH_2$ |
| [RuH{PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | 205.6 (t, 14) | 162.3 (s) | | | | | | |
| | Me | 206.0 (t, 13) | 163.1 (s) | | | | | 19.4 (s) | |
| | Et | 205.7 (t, 15) | 167.5 (s) | | | | | 10.5 (s) | 22.9 (s) |
| | Ph | 205.6 (t, 15) | 163.2 (s) | 133.1 (s) | 129.6 (s) | 128.0 (s) | 126.8 (s) | | |
| [RuCl{PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | 206.4 (t, 14) | 152.3 (s) | | | | | | |
| | Me | 206.0 (t, 14) | 164.7 (t, 3) | | | | | 17.5 (s) | |
| | Et | 206.3 (t, 15) | 168.8 (5) | | | | | 10.1 (s) | 22.1 (s) |
| [Ru($O_2CCF_3$){PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H[b] | 206.3 (t, 14) | 152.1 (s) | | | | | | |
| | Me[b] | 205.7 (t) | 164.2 (s) | | | | | 16.2 (s) | |
| | Ph[b] | 204.9 (dd, 15, 17) | 173.0 (s) | 134.1 (d, 9) | 130.9 (s) | 128.3 (s) | 127.5 (s) | | |
| [OsH{PhNC(R)NPh}(CO)($PPh_3$)$_2$] | Me | 186.8 (t, 10) | 163.5 (s) | | | | | 21.0 (s) | |
| | Et | | 167.9 (s) | | | | | 10.6 (s) | 24.6 (s) |
| | Ph | 185.6 (t, 11) | 164.1 (s) | | 129.7 (s) | 128.3 (s) | 126.8 (w) | | |
| [OsCl{PhNC(R)NPh}(CO)($PPh_3$)$_2$] | H | 183.0 (t, 10) | 153.4 (t, 3) | | | | | | |
| | Ph | 183.9 (t, 11) | 165.9 (s) | 131.8 (s) | 130.0 (s) | 126.9 (s) | 126.7 (s) | | |
| [Os($O_2CCF_3$){PhNC(R)NPh}(CO)($PPh_3$)$_2$] | Et[c] | 182.3 (t, 10) | 180.0 (s) | | | | | 10.1 (s) | 23.0 (s) |
| | Ph[b] | | 174.8 (s) | | | | | | |
| [IrH(Cl){PhNC(R)NPh}($PPh_3$)$_2$] | H | | 154.4 (s) | | | | | | |
| | Me | | 166.3 (s) | | | | | 21.8 (s) | |
| | Et | | 171.2 (s) | | | | | 10.8 (s) | 24.8 (s) |
| | Ph | | 167.6 (s) | 134.6 (s) | 128.8 (s) | 127.4 (s) | 128.8 (s) | | |
| [$IrH_2${PhNC(R)NPh}($PPh_3$)$_2$] | Ph | | 164.9 (s) | | 129.7 (s) | 128.0 (s) | 127.4 (s) | | |

[a] Chemical shift data in ppm relative to $SiMe_4$; s = singlet, d = doublet, t = triplet. Coupling constants (Hz) given in parentheses. [b] δ($CF_3CO_2$) lost in background. [c] δ($CF_3CO_2$) 114.8 (q), $^2J_{CF}$ = 292 Hz; δ($CF_3CO_2$) 162.0 (q), $^3J_{CF}$ = 36 Hz.

the relatively poor co-ordinating power of the carboxylate anions militate against carbonyl abstraction and bis(chelate) formation respectively. In contrast, the 1,3-diaryltriazenes are basic but given their strong chelating tendency prefer to form bis(chelates) rather than promote carbonyl abstraction. However, for the *N,N'*-diphenylamidines which are likely to be marginally more basic and less readily deprotonated than their triazene counterparts, the balance is tilted in favour of carbonyl abstraction rather than bis(chelate) formation. The apparent formation of a carbonyl-free bis(chelate) [Ru{PhNC(Me)NPh}$_2$($PPh_3$)$_2$] from [$RuH_2$($PPh_3$)$_4$] and *N,N'*-diphenylacetamidine may simply reflect the balance of basicity and co-ordinating power for this particular amidine. However, the insolubility of the product, which precludes its crystallisation or full spectroscopic characterisation, is not typical for compounds of this general stoichiometry made by the carbodiimide-insertion route,[6] and may be indicative of a different formulation. One formulation which is in accord with the analytical data is the hydride [RuH{PhNC(Me)NPh}{PhNC(Me)NHPh}($PPh_3$)$_2$]- which might be formed by displacement of phosphine from the intermediate [RuH{PhNC(Me)NPh}($PPh_3$)$_3$] and deposited by virtue of its low solubility. Unfortunately the infrared spectrum shows no evidence of ν(RuH) or ν(NH) absorptions and thus offers no support for this suggestion.

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