Carbene Complexes. Part V.[1] Imidoyl Chlorides as Synthetic Reagents, and the Preparation of Rhodium(III) Carbene Complexes from Rhodium(I) Precursors

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A new transition-metal carbene synthesis is described. Thus, rhodium(III) complexes $[Cl_3(L)Rh{-}C(R^1)NHR^2]$ [R^1 = Ph with R^2 = Me, Et, or Pr^i; or R^1 = Me and R^2 = $C_6H_4{\cdot}Me$-*o*; L = (tertiary phosphine)$_2$, (tertiary phosphine) (CO), or CO] are prepared by the reaction of an imidoyl chloride with a rhodium(I) substrate in the presence of hydrogen chloride. Mechanisms are discussed.

EARLIER Parts have dealt with carbene complexes of palladium(II) and platinum(II), obtained by nucleophilic attack of electron-rich olefins upon halogen-bridged metal(II) substrates: synthetic procedures were described in Part I,[2] chemical behaviour in Part II,[3] ^{13}C n.m.r. spectra in Part III,[4] and other spectroscopic features in Part IV.[1] Our initial objective in metal carbene chemistry was to devise syntheses involving organic precursors, rather than to employ a metal carbonyl, isonitrile, or related complex as the source of the $M{-}C_{carb}$ bond.[5] This paper describes a second approach to the problem (see Table for the new complexes). The organic starting materials are imidoyl chlorides, $RC(Cl){=}NR^1$,[6] the nitrogen analogues of acyl chlorides. The latter have featured prominently as reagents in transition-metal organometallic chemistry,[7] whereas the former were previously unexplored; a preliminary communication of the present work has been published,[8] and another [9] described some consequential experiments.

An imidoyl chloride is readily prepared by the action of a powerful chlorinating agent on the appropriate mono-*N*-substituted amide. Phosphorus pentachloride [equation (1)] was particularly convenient for the chlorides used (R = Ph with R^1 = Me, Et, or Pr^i; or R^1 = *o*-Me·C_6H_4 with R = Me or Et).[10] Only *ca.* 30%

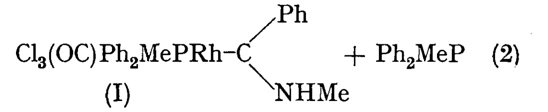
$$RCONHR^1 + PCl_5 \longrightarrow RC(Cl){=}NR^1 + POCl_3 + HCl \quad (1)$$

yields were obtained for a derivative of a straight-chain aliphatic acid, while for the benzamide derivatives yields were almost quantitative. A hydrogen atom in a position α to chlorine allows competitive reactions of condensation and formation of a ketenimine by elimination of hydrogen chloride.[6] The presence of an *o*-tolyl group somewhat inhibits condensation reactions since attack at nitrogen is sterically hindered.

Spectral data for the imidoyl chlorides used in this study are shown in the Table. Also included are data for *N*-(*o*-tolyl)propionimidoyl chloride; this compound was not prepared analytically pure owing to the continuing presence of an impurity indicated by its n.m.r. spectrum to be $MeCH{=}C{=}N{\cdot}C_6H_4{\cdot}Me$-*o* [τ (Me) 8·73d, *J* 6·6 Hz; τ (*o*-Me) 7·92s; τ (CH) 5·32q, *J* 6·6 Hz]. The compound, $EtC(Cl){=}NC_6H_4Me$-*o*, was useful only in confirming that the high-field methyl n.m.r. resonance of $MeC(Cl){=}NC_6H_4Me$-*o* is due to the *o*-methyl group.

The reaction of, for example, $(Ph_2MeP)_2Rh(CO)Cl$ with *N*-methylbenzimidoyl chloride in dichloromethane was followed by observing changes in the carbonyl stretching mode. Use of dry dichloromethane as solvent resulted in a very slow reaction, whereas the unpurified solvent afforded a product after 24 h. The same compound [equation (2)] was obtained immediately upon bubbling hydrogen chloride through the solution. The observation with unpurified solvent is therefore attributed to formation of hydrogen chloride by hydrolysis of an imidoyl chloride in a wet solvent. As no immediate reaction takes place between $(Ph_2MeP)_2Rh(CO)Cl$ and HCl, it may be that an iminium salt $[PhC(Cl)NHMe]^+Cl^-$ is the reactive species (*cf.* ref. 9). Reaction (2) opens up many other possibilities using related halides [6,9] such as chloroformimidates, $ROC(Cl){=}NR^1$, or chloroformamidinium salts, *e.g.*, $[Me_2NC(Cl)NMe_2]^+Cl^-$.

$$(Ph_2MeP)_2Rh(CO)Cl + PhC(Cl){=}NMe + HCl \longrightarrow$$



$$Cl_3(OC)Ph_2MePRh{-}C\begin{smallmatrix}Ph\\ NHMe\end{smallmatrix} + Ph_2MeP \quad (2)$$

(I)

The carbene complex (I) was identified by elemental analyses (Table) and by its i.r. and n.m.r. spectra (Table), discussed below. An isoelectronic cation, $[I(Ph_3P)_2Pt{-}C(Ph)NHMe]^+PF_6^-$, has been obtained [11] by protonation of the imidoyl nitrogen in $I(Ph_3P)_2Pt{-}C(Ph){=}NMe$ by use of $NH_4^+PF_6^-$. The imidoyl complex $Cl(Ph_3P)_2PtC(Ph){=}NMe$ has been obtained by oxidative addition of $PhC(Cl){=}NMe$ to $(Ph_3P)_4Pt$.[12]

An improved yield of another carbene complex (II),

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[1] Part IV, D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *J. Organometallic Chem.*, submitted for publication.

[2] Part I, D. J. Cardin, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 514.

[3] Part II, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 906.

[4] Part III, D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, 1982.

[5] *Cf.* D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

[6] *Cf.* H. Ulrich, ' The Chemistry of Imidoyl Halides,' Plenum Press, New York, 1968.

[7] *Cf.* A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597; A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 243.

[8] M. E. Lappert and A. J. Oliver, *J.C.S. Chem. Comm.*, 1972, 274.

[9] B. Çetinkaya, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1972, 851.

[10] J. von Braun and H. Silvermann, *Ber.*, 1930, **63**, 498; J. von Braun and W. Pinkernelle, *ibid.*, 1934, **67**, 1218.

[11] P. M. Treichel, J. J. Benedict, R. W. Hess, and J. P. Stenson, *Chem. Comm.*, 1970, 1627.

[12] M. F. Lappert and J. McMeeking, to be published.

$Cl_3(OC)Ph_3PRhC(Ph)NHMe$, was obtained by using $[Ph_3PRh(CO)Cl]_2$ in place of $(Ph_2MeP)_2Rh(CO)Cl$. In this reaction CO is displaced instead of Ph_3P [*cf.* equation (2)] and this makes for easier purification of the product. Related complexes (III), (IV), and (V) were obtained from $[Ph_3PRh(CO)Cl]_2$, hydrogen chloride, and respectively the chlorides $PhC(Cl){=}NEt$, $PhC(Cl){=}NPr^i$, and $MeC(Cl){=}N{\cdot}C_6H_4{\cdot}Me\text{-}o$. The solvent used for these reactions was benzene; although this is difficult to remove from the products, it is superior in this respect to dichloromethane. Only for compound (VI) is a stoicheiometric quantity of dichloromethane associated with a tertiary phosphine-substituted product, and this causes minor changes in its solid-state i.r. spectrum [see ν(NH) and ν(RhCl), Table].

	Compound	M.p. (t/°C)	Colour	Yield (%)	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
(I)	$Cl_3(OC)Ph_2MePRh{-}C(Ph)NHMe$ [a]	160—163	White	42	47·8	4·1	2·7	47·5	3·98	2·56
(II)	$Cl_3(OC)Ph_3PRh{-}C(Ph)NHMe$	168—171	White	85	52·9	4·1	2·25	52·4	3·91	2·26
(III)	$Cl_3(OC)Ph_3PRh{-}C(Ph)NHEt$ [b]	164—167	White	65	53·3	4·35	2·25	53·1	4·14	2·21
(IV)	$Cl_3(OC)Ph_3PRh{-}C(Ph)NHPr^i$	162—164	White	79	53·6	4·75	2·15	53·8	4·36	2·17
(V)	$Cl_3(OC)Ph_3PRh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}o$ [c]	>200	White	47	53·1	4·2	2·25	53·1	4·14	2·21
(VI)	$Cl_3(OC)Ph_3PRh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}oCH_2Cl_2$	>200 [d]	Pale yellow	76	48·8	4·1	1·9	48·5	3·93	1·95
(VII)	$[Cl_3(OC)Rh{-}C(Ph)NHMe]_n$	>190 decomp.	Yellow	46	30·6	2·75	3·8	30·3	2·55	3·93
(VIII)	$[Cl_3(OC)Rh{-}C(Ph)NHPr^i]_n$	>160 decomp.	Yellow	59	34·4	3·7	3·35	34·4	3·41	3·64
(IX)	$[Cl_3(OC)Rh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}o]_n$	>200 decomp.	Orange-yellow	49	32·0	3·4	3·3	32·3	3·20	3·77
(X)	$Cl_3(Me_2PhP)_2Rh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}o$	289—291	Yellow	29	48·9	5·55	2·5	48·5	5·38	2·26

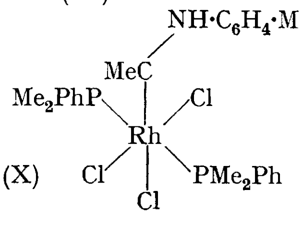
	Compound	I.r. data [e] ν(NH)	ν(CO)	ν(CN)	ν(RhCl₃)	N.m.r. data [f] τ (Ph) [g]	τ (NCH)	τ (CMe)	τ (o-Me)	τ (P-Me)
	$PhC(Cl){=}NMe$			1675		2·72	6·63s			
	$PhC(Cl){=}NEt$			1665		2·70	6·30q (J 7·4)	8·70t (J 7·4)		
	$PhC(Cl){=}NPr^i$			1664		2·67	5·88sept (J 6·3)	8·73d (J 6·3)		
	$MeC(Cl){=}NC_6H_4Me\text{-}o$			1695		3·03		7·55s	7·92s	
	$EtC(Cl){=}NC_6H_4Me\text{-}o$			1700		3·01		8·73t [h] (J 7·4)	7·92s	
(I)	$Cl_3(OC)Ph_2MePRh{-}C(Ph)NHMe$	3135	2100	1607	324m, 285s	2·52	7·03d (J 5·2)			7·42d (J 12·8)
(II)	$Cl_3(OC)Ph_3PRh{-}C(Ph)NHMe$	3120	2105	1598	324m, 293s	2·63	7·10d (J 4·8)			
(III)	$Cl_3(OC)Ph_3PRh{-}C(Ph)NHEt$	3130	2105	1599	330w, 299m, 283w	2·57	6·75m (J 7·4)	8·80t (J 7·4)		
(IV)	$Cl_3(OC)Ph_3PRh{-}C(Ph)NHPr^i$	3100	2100	1596	324m, 286s	2·65	6·52m	8·78d (J 6·4)		
(V)	$Cl_3(OC)Ph_3PRh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}o$	3140	2105	1560	287broad	2·52		7·52s	7·67s	
(VI)	$Cl_3(OC)Ph_3PRh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}oCH_2Cl_2$ [i]	3095	2105	1571	306m, 297m, 273m	2·52		7·52s	7·67s	
(VII)	$[Cl_3(OC)Rh{-}C(Ph)NHMe]_n$	3165	2120	1612	355m, 340w, 324w, 297w					
(VIII)	$[Cl_3(OC)Rh{-}C(Ph)NHPr^i]_n$	3110	2120	1602	360s, 320m, 301w, 255m					
(IX)	$[Cl_3(OC)Rh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}o]_n$	3115	2125	1570	369m, 355w, 325m, 304m, 288m, 252m					
(X)	$Cl_3(Me_2PhP)_2Rh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}o$ [j]	3110		1529	330m, 301w, 273m	2·77		8·27s	7·93s	7·93t (J 8·4) [k]

[a] Cl analysis, Found: 19·2; reqd.: 19·1%. [b] *M*, Found: 607; reqd.: 633. [c] Cl analysis, Found: 16·3; reqd. 16·8%; P analysis, Found: 4·85, reqd.: 4·89%. [d] Compound loses solvent at lower temperature. [e] I.r. spectra obtained in Nujol mull, values in cm⁻¹. [f] Measured in $CDCl_3$ soln., tetramethylsilane internal standard. Coupling constants reported in Hz. [g] Complex resonances, chemical shift of most intense line recorded. [h] Quartet observed at τ 7·30 (*J* 7·4). [i] Singlet observed at τ 4·70 due to dichloromethane. [j] A very broad resonance at τ 5·00, presumed due to N–H. [k] $J = J(P_1) + J(P_2)$ = separation of outer peaks of triplet.[16]

The use of di-μ-chloro-tetracarbonyldirhodium(I), $[(OC)_2RhCl]_2$, similarly afforded the Rh^{III} carbene complexes (VII)—(IX), which are presumed to be dimeric or polymeric because of their insolubility and the complexity of the i.r. spectra in the $\nu(RhCl_3)$ region. A soluble derivative, (X), of (IX) was obtained [equation (3)].

$$\frac{1}{n}[Cl_3(OC)Rh{-}C(Me)NH{\cdot}C_6H_4{\cdot}Me\text{-}o]_n + 2Me_2PhP \longrightarrow$$

(IX)



(X)

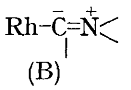
+CO (3)

The more important i.r. absorption bands, measured for the new compounds, are listed in the Table. An N–H stretching mode is always observed between 3165 and 3095 cm⁻¹. This is clearly a very low value but is consistent with most other Pd^{II} or Pt^{II} carbene complexes containing the moiety (A).[13] By contrast, CO stretching modes for the rhodium carbonyl derivatives are at relatively high wavenumber, typical of Rh^{III} with electron-withdrawing substituents. The value of ν(CO) for (II) is similar to the value of 2111 cm⁻¹ reported for $Cl_3(OC)_2Ph_3PRh$ [14a] (in another study[15] the values 2100w and 2073s cm⁻¹ were reported).

The carbon–nitrogen double bonds of imidoyl chlorides typically absorb around 1700 cm⁻¹.[6] Only a small decrease in this value occurs upon conversion into the formally C–N single bond of the corresponding carbene complex. This is consistent with the view that in aminocarbene complexes there is considerable $C_{carb}N$ multiple bonding,[5] as in (B). Low electron density on nitrogen also accounts for the low values of ν(N–H).

$$M{-}\overset{|}{C}{-}\overset{|}{N}{-}H$$

(A)



$$Rh{-}\overset{-}{C}{=}\overset{+}{N}\!\!<$$

(B)

¹H N.m.r. data are in the Table, including results for the imidoyl chloride precursors; such information seems

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[13] E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 21; B. Crociani and T. Boschi, *J. Organometallic Chem.*, 1970, **24**, C1.

[14] (*a*) G. Deganello, P. Uguagliti, B. Crociani, and U. Belluco, *J. Chem. Soc.* (*A*), 1969, 2726; (*b*) R. Poilblanc and J. Gallay, *J. Organometallic Chem.*, 1971, **27**, C53.

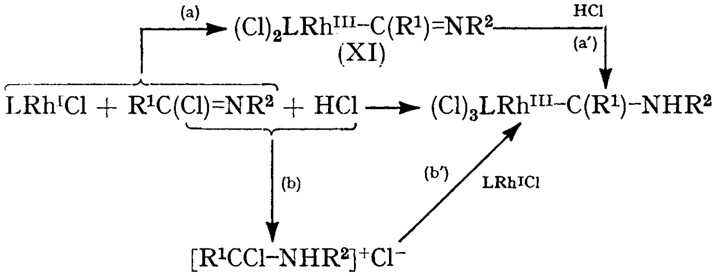
[15] B. F. G. Johnson, J. Lewis, and P. W. Robinson, *J. Chem. Soc.* (*A*), 1970, 1100.

not to have been previously available. Generally, the spectra are consistent with suggested structures and, for the rhodium complexes, are similar to the spectra of the parent imidoyl chloride. Compounds (I)—(IV) show splitting of the resonances of C–H protons α to an amino-proton; it seems most likely that this splitting may be ascribed to coupling of the single amino-proton, but coupling to phosphorus cannot be completely ruled out. The resonances of the amino-protons were not observed, presumably owing to broadening by the nitrogen quadrupole as well as coupling of other protons. In (X), however, where no coupling of the amino-proton to other protons is likely, a broad resonance integrating to one proton was observed at τ 5·00.

The two dimethylphenylphosphine ligands in compound (X) may be assigned as mutually *trans*, because a triplet is observed for the P–Me resonance.[16]

Integration results for all ^1H n.m.r. spectra reported here were consistent with the suggested structures.

The mechanism of reactions such as that shown in equation (2) may involve either or both of the generalised pathways 4(a, a′) or 4(b, b′). There is independent evidence for each of the steps 4(a), 4(a′), 4(b), and (4b′). Pathway 4(b, b′) has been termed an example of a three-fragment oxidative addition;[8,9] other cases include the conversion of Ir^I complexes into RIr^{III}(CO)Cl adducts with RCOCl,[17] and of Rh^I complexes to $(Cl)_2Rh^{III}$–C(R^1)–N(R^2)–C(R^1)=NR^2, with imidoyl chlorides in the rigorous absence of HCl.[8,18]



(4)

EXPERIMENTAL

Reactions were carried out under nitrogen; when required, dry dichloromethane was freshly distilled from phosphorus(v) oxide. Benzene and diethyl ether were stored over sodium.

N-(*o*-Tolyl)acetimidoyl chloride and *N*-methylbenzimidoyl chloride were prepared by published methods.[10] A procedure analogous to that employed for PhC(Cl)=NMe was also used to prepare PhC(Cl)=NEt [b.p. 98 °C/12 mmHg,[19] 73% (Found: C, 64·4; H, 6·05; N, 8·20. Calc. for $C_9H_{10}ClN$: C, 64·5; H, 6·01; N, 8·21%)] and PhC(Cl)=NPr^i [b.p. 100 °C/10 mmHg,[19] 81% (Found: C, 66·3; H, 6·55; N, 7·9. Calc. for $C_{10}H_{12}ClN$: C, 66·1; H, 6·66; N, 7·71%)].

The complex [Rh(CO)$_2$Cl]$_2$ was obtained by an established method.[20] Treatment of this with the stoicheiometric quantity of tertiary phosphine afforded the complexes [Ph$_3$PRh(CO)Cl]$_2$ [14] and (Ph$_2$MeP)$_2$Rh(CO)Cl.

Molecular weights were obtained in chloroform solution with a Mechrolab osmometer, and analyses (Table) by the microanalytical laboratory of this department. ^1H N.m.r. spectra were recorded on a Varian T60 spectrometer, and i.r. spectra (polystyrene calibration), on a Perkin-Elmer 457 spectrometer.

Preparation of Cl$_3$(OC)Ph$_2$MePRh–C(Ph)NHMe (I).—A solution of (Ph$_2$MeP)$_2$Rh(CO)Cl (0·341 g, 0·60 mmol) in dichloromethane (15 ml) was saturated with hydrogen chloride and a solution of *N*-methylbenzimidoyl chloride (0·423 g, 2·76 mmol) also in dichloromethane (5 ml) was introduced. After two days at room temperature, diethyl ether (40 ml) was added, and the solution cooled to −15 °C. Recrystallisation of the resulting product from dichloromethane–diethyl ether gave colourless needles of the *complex* (I) (0·143 g, 42%), freed from solvent by crushing and storing under high vacuum for several days.

Preparation of Cl$_3$(OC)Ph$_3$PRh–C(Ph)NHMe (II) *and of Compounds* (III), (IV), *and* (V).—A solution of *N*-methylbenzimidoyl chloride (0·195 g, 1·27 mmol) in benzene (5 ml) was added to [Ph$_3$PRh(CO)Cl]$_2$ (0·155 g) in benzene (15 ml). Hydrogen chloride gas was passed through the stirred mixture, and the yellow suspension changed to a white crystalline precipitate. After 15 min, diethyl ether (20 ml) was added and the mixture set aside for 2 h. Filtration and drying under high vacuum for one week gave the *complex* (II) (0·177 g, 85%).

The closely related *compounds* Cl$_3$(OC)Ph$_3$PRh–C(Ph)-NHEt (III), Cl$_3$(OC)Ph$_3$PRh–C(Ph)NHPr^i (IV), and Cl$_3$-(OC)Ph$_3$PRh–C(Me)NH·C$_6$H$_4$·Me-*o* (V), were also prepared by this method by use of the appropriate imidoyl chloride. In these cases, the reaction mixture was set aside for 48 h instead of the 2 h employed in the above procedure.

Preparation of Cl$_3$(OC)Ph$_3$PRh–C(Me)NH·C$_6$H$_4$·Me-*o*CH$_2$-Cl$_2$ (VI).—Dicarbonylchloro(triphenylphosphine)rhodium(I) dimer [14a] (0·11 g) was dissolved in dichloromethane (10 ml) and the solution was saturated with hydrogen chloride by bubbling the gas through the mixture for 10 min. Addition of a solution of *N*-(*o*-tolyl)acetimidoyl chloride (0·12 g, 0·73 mmol) in dichloromethane (5 ml) caused an immediate change to a paler shade of yellow. After reduction of the volume of solvent to 10 ml, diethyl ether (20 ml) was added to yield pale yellow crystals of the complex (VI) (0·267 g, 76%).

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[16] *Cf.* A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597.

[17] B. L. Shaw and E. Singleton, *J. Chem. Soc.* (*A*), 1967, 1683; R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 1970, 4331; M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, 1971, **93**, 1368; *Inorg. Chem.*, 1972, **11**, 469.

[18] Part VI, P. B. Hitchcock, M. F. Lappert, G. M. McLaughlin, and A. J. Oliver, following paper.

[19] I. Ugi, F. Beck, and U. Fetzer, *Chem. Ber.*, 1962, **95**, 126.

[20] J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

Preparation of $[Cl_3(OC)Rh{-}C(Ph)NHMe]_n$ (VII).—A solution of $[Rh(CO)_2Cl]_2$ (0·217 g, 0·558 mmol) in dichloromethane (10 ml) was saturated with hydrogen chloride by bubbling the gas through the solution for 10 min. A solution of *N*-methylbenzimidoyl chloride (0·36 g, 2·34 mmol) also in dichloromethane (5 ml) was added and the mixture was set aside for 2 days. The yellow microcrystalline precipitate which formed was filtered off (0·151 g). Addition of diethyl ether (30 ml) to the filtrate gave a further quantity (0·033 g) of the required *complex* (VII).

Preparation of $[Cl_3(OC)Rh{-}C(Ph)NHPr^i]_n$ (VIII).—Di-μ-chloro-tetracarbonyldirhodium(I) (0·204 g, 0·53 mmol) was dissolved in dichloromethane (20 ml). To this solution, *N*-(2-propyl)benzimidoyl chloride (0·672 g, 3·70 mmol) in dichloromethane (5 ml) was added. The mixture was set aside for 16 h and diethyl ether (70 ml) was then very slowly added. Yellow crystals of the pure *complex* (VIII) (0·219 g, 59%) were collected and dried.

Preparation of $[Cl_3(OC)Rh{-}C(Me)NH{\cdot}C_6H_4Me]_n$ (IX).—*N*-(*o*-Tolyl)acetimidoyl chloride (0·22 g, 1·31 mmol) dissolved in diethyl ether (10 ml) was added to a solution of $[Rh(CO)_2Cl]_2$ (0·196 g, 0·499 mmol) in dichloromethane (15 ml). After 48 h at 20 °C and cooling to 0 °C, orange-yellow crystals of the *complex* (IX) (0·181 g, 49%) were collected.

Preparation of $Cl_3(Me_2PhP)_2Rh{-}C(Me)NH{\cdot}C_6H_4Me\text{-}o$ (X).—Dimethylphenylphosphine (0·126 g, 0·912 mmol) was dissolved in dichloromethane (20 ml). Addition of (IX) led to evolution of gas. After 16 h, the mixture was evaporated to dryness and extracted with hot toluene (20 ml). Reduction of the volume of solution to 5 ml and addition of diethyl ether (25 ml) afforded yellow crystals of the *complex* (X) (0·095 g, 29%).

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