Methyleneamido-complexes of Rhenium

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Alkylimido-complexes $[ReCl_3(NR)(PR'_3)_2]$ (PR'_3 = tertiary phosphine) react with bases such as pyridine to yield methyleneamido-complexes, which contain the group –N=CHR (R = H or alkyl). Acids reconvert the methyleneamido-complexes into alkylimido-complexes.

THE methyleneamide and substituted methyleneamide anions $[N{=}CR_2]^-$ (R = alkyl or hydrogen) have a potential to bind to transition metals in two ways, as have, for example, NO and aryldiazenide ions. As a ' one-electron donor ', there would be a lone pair of electrons situated on the nitrogen and the M–N–C atom chain should be bent. As a ' three-electron donor ' the M–N–C chain should be linear.

However, no general survey of methyleneamido-complex chemistry has yet been possible, primarily due to the paucity of general preparative methods. Substituted methyleneamido-complexes are generally prepared by the reactions of lithium ketimides, LiNCRR′ (R and R′ are the same or different alkyl or aryl groups), or occasionally ketimines, with metal halido-complexes.[1] Alternatively, trialkylstannyl derivatives, such as $Me_3Sn-N=C(CF_3)_2$, can also be used in metathetical reactions.[2] However, hitherto there has been no preparative route to the complexes of the unsubstituted methyleneamido-ligand $N=CH_2$. In a preliminary communication [3] we described how the methylimido-ligand in the complexes [4] $[ReCl_3(NMe)(PPh_2R)_2]$ (R = Me, Et, or Ph) may be reversibly deprotonated by, for example, an excess of pyridine (py) to yield $[ReCl_2(NCH_2)(py)(PPh_2R)_2]$. Here we detail and extend that earlier report.

TABLE 1

Infrared and ^1H n.m.r. spectra of the methyleneamido- and alkylimido-complexes

Complex	Resonance (τ) of alkyl or alkylene protons of alkylimido- or methyleneamido-groups	ν(N=C) or [a] typical Re=NR bands (cm⁻¹)	ν̃(Re–Cl) [a]/cm⁻¹
$[ReCl_2(NCH_2)(py)(PMePh_2)_2]$	11.15(2), 1 : 2 : 1 (t) [b]	1 585m	305m, 275m
$[ReCl_2(NCH_2)(py)(PEtPh_2)_2]$	11.38(2), 1 : 2 : 1 (t) [b]	1 585m (sh)	300m, 268m
$[ReCl_2(NCH_2)(py)(PPh_3)_2]$	11.49(2), 1 : 2 : 1 (t) [b]	1 592w	305m, 268m
$[ReCl_2(NCH_2)(PMe_2Ph)_3]$	11.27(2), two 1 : 2 : 1 (t) [b]	1 560m (sh)	250w
$[ReCl_2(NCHMe)(py)(PPh_3)_2]$	6.60(3), 1 : 1 (d); 11.15(1) (n) (1 : 2 : 4 : 6 : 6 : 6 : 4 : 2 : 1) [c]	*d*	310m, 260w
$[ReCl_2(NCHEt)(py)(PPh_3)_2]$	9.12(3), 1 : 2 : 1 (t); 5.75(2) (o); 11.01(1) (s) [c]	*d*	300m, 250w
$[ReCl_2(NMe)(py)(PEtPh_2)_2]Cl$	7.4(3), 1 : 2 : 1 (t) [b]	*e*	310m (sh), 280m
$[ReCl_2(NEt)(py)(PEtPh_2)_2][SFO_3]$	8.31(3), 1 : 2 : 1 (t); 7.77(2) (m) [b]	*e*	318m, 272m
cis, fac-$[ReCl_3(NMe)(PMe_2Ph)_2]$ [f]	9.25(3), 1 : 2 : 1 (t) [b]	1 310m	268s, 282s, 314s
trans-$[ReCl_3(NMe)(PMe_2Ph)_2]$	9.76(3), 1 : 2 : 1 (t) [b]	1 318m	260m, 300s
cis, fac-$[ReCl_3(NMe)(PMePh_2)_2]$ [f]	9.53(3), 1 : 2 : 1 (t) [b]	1 319m	
trans-$[ReCl_3(NMe)(PMePh_2)_2]$	9.03(3), 1 : 2 : 1 (t) [b]	1 302m	

[a] Nujol mulls. [b] In dichloromethane solution. [c] In benzene–pyridine solution. [d] Not detected. [e] Not identified. [f] Phosphine alkyl-proton resonances show that the phosphines are *cis*. The triplets for NCH_3 protons show that the chlorines must be *fac*.

RESULTS AND DISCUSSION

The initial aim of our work was to displace the alkylimido-ligand (NR) from alkylimido-complexes $[ReCl_3(NR)(PR_3)_2]$ (PR_3 = tertiary phosphine) by an uncharged ligand to generate an alkylnitrene. Ligands such as carbon monoxide, nitrogen oxide, methyl cyanide, and pyridine were tried but we obtained no evidence that the nitrene was liberated by them.

Carbon monoxide reacted with *trans*-$[ReCl_3(NR)(PPh_3)_2]$ (R = Me or Et) in boiling toluene to yield the known complexes *cis*- and *trans*-$[Re(CO)_3Cl(PPh_3)_2]$ [5] as the principal solid products. For R = Me, the yields were **14** and 60%, respectively, but some bridged carbonyl species were also formed. Hydrogen cyanide and hydrogen chloride were detected among the volatile reaction products, but no methyl isocyanate, which might be expected if methylnitrene, ligating or free, had reacted with CO. The complex *trans*-$[ReCl_3(NMe)(PPh_2CH_2CMe=CH_2)_2]$ reacted with CO under more vigorous conditions (10 h at toluene reflux), and the only products detected were $[Re(CO)_3Cl(PPh_2CH_2CMe=CH_2)_2]$ and hydrogen cyanide. The reaction of $[ReCl_3(NMe)(PPh_2CH_2CH=CH_2)_2]$ in boiling toluene with CO yielded no identifiable products, and *trans*-$[ReCl_3(NPh)(PPh_2R)_2]$ (R = Ph or $CH_2CH=CH_2$) and *cis*- and *trans*-$[ReCl_3(NMe)(PMe_2Ph)_2]$ did not react with CO under a variety of reaction conditions.

The production of hydrogen cyanide, apparently derived from the NMe group, and the simultaneous loss of two chlorine atoms from the rhenium suggested that successive dehydrohalogenations had occurred. We therefore investigated the reactions of the alkylimido-complexes with bases. We found that pyridine at 20 °C dehydrohalogenates *trans*-$[ReCl_3(NMe)(PPh_2R)_2]$ (R = Ph, Me, or Et) to form methyleneamido-complexes $[ReCl_2(NCH_2)(py)(PPh_2R)_2]$ and pyridine hydrochloride. The complex *cis,fac*-$[ReCl_3(NMe)(PMePh_2)_2]$ underwent an analogous reaction. The green products reacted with hydrogen chloride to yield small quantities of starting material, but the major product from the reaction of $[ReCl_2(NCH_2)(py)(PPh_2Et)_2]$ in benzene solution was the ionic complex $[ReCl_2(NMe)(py)(PPh_2Et)_2]Cl$. Heating the latter complex *in vacuo* then regenerated the parent neutral methylimido-complex.

We were unable to remove a second molecule of hydrogen halide from the methylimido-complexes to obtain complexes of hydrogen cyanide, even using pyridine at reflux or 2,2′-bipyridyl. The monodehydrohalogenation reaction also occurred with the higher homologues, and $[ReCl_3(NR)(PPh_3)_2]$ (R = Et or Prⁿ) reacted with pyridine in benzene solution to afford green air-stable solids $[ReCl_2(N=CHMe)(py)(PPh_3)_2]$ or $[ReCl_2(N=CHEt)(py)(PPh_3)_2]$. These higher alkylimido-complexes react very

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[1] M. Kilner and J. N. Pinkney, *J. Chem. Soc.* (*A*), 1971, 2887.

[2] J. Keable, D. G. Othen, and K. Wade, *J.C.S. Dalton*, 1976, 1.

[3] J. Chatt, R. J. Dosser, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 1243.

[4] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc.* (*A*), 1970, 2239.

[5] P. G. Douglas and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1491; J. Chatt, J. R. Dilworth, H. P. Gunz, and G. J. Leigh, *J. Organometallic Chem.*, 1974, **64**, 245.

much faster than the methylimido-complexes, and the corresponding methyleneamido-products are much less stable and more difficult to purify.

TABLE 2

New alkylimido-, arylimido-, and methyleneamido-complexes of rhenium

Complex	Configuration	Colour	M [a]	Analyses (%) [a] C	H	N	Cl	Λ S cm^2 mol^{-1}	M.p. (θ_c/°C)
$[ReCl_3(NMe)(PPh_2CH_2CH{=}CH_2)_2]$	*trans*-P	Blue	762 (744) [b]	48.1 (48.1)	4.4 (4.3)	1.9 (1.8)	13.4 (13.7)	0 [d]	209—210
$[ReCl_3(NMe)(PPh_2CH_2CMe{=}CH_2)_2]$ [c]	*trans*-P	Blue	773 (802) [b]	49.1 (49.4)	4.4 (4.6)	2.0 (1.8)	12.6 (12.9)	0 [d]	205—206
$[ReCl_3(NMe)(PMe_2Ph)_2]$	*trans*-P	Blue	603 (598) [b]	34.1 (34.1)	4.2 (4.2)	2.5 (2.3)	18.0 (17.8)	0 [e]	250—252
	cis-P	Violet	592 (598) [b]	33.8 (34.1)	4.2 (4.2)	2.4 (2.3)	18.0 (17.8)	0 [e]	243—247
$[ReCl_3(NMe)(PMePh_2)_2]$	*trans*-P	Blue	698 (722) [b]	45.1 (44.9)	4.2 (4.1)	2.0 (1.9)	15.3 (14.7)	0 [e]	232—234
	cis-P	Violet	703 (722) [b]	45.0 (44.9)	4.2 (4.1)	2.0 (1.9)	14.4 (14.7)	0 [e]	237—238
$[ReCl_3(NEt)(PMePh_2)_2]$	*trans*-P	Blue	764 (736) [b]	45.7 (45.7)	4.4 (4.3)	2.0 (1.9)	14.1 (14.5)	0 [e]	231—233
$[ReCl_2(NMe)(py)(PEtPh_2)_2]Cl$	*trans*-P	Violet		48.9 (49.2)	4.7 (4.6)	3.1 (3.4)	13.2 (12.8)	73.5 [d]	101—103 (decomp.) [f]
$[ReCl_2(NMe)(py)(PEtPh_2)_2][BF_4]$	*trans*-P	Violet		46.3 (46.4)	4.4 (4.3)	3.2 (3.2)		83.5 [d]	123—124 [f]
$[ReCl_2(NMe)(PMe_2Ph)_3]Cl$	*mer*-P	Pink		41.1 (40.8)	5.0 (4.9)	2.0 (1.9)	14.8 (14.4)	85.8 [d]	148 (decomp.) [f]
$[ReCl_2(NEt)(py)(PEtPh_2)_2][SFO_3]$ [c]	*trans*-P	Violet		46.9 (46.4)	4.7 (4.4)	3.1 (3.1)		90.0 [d]	115 [f]
$[ReCl_3(NPh)(PPh_2CH_2CH{=}CH_2)_2]$ [c]	*trans*-P	Green	810 (836) [b]	52.1 (51.7)	4.4 (4.2)	1.7 (1.7)		0 [e]	
$[ReCl_3(NPh)(py)_2]$	probably *trans*-py	Green		35.3 (35.5)	2.7 (2.8)	7.6 (7.7)	20.1 (19.6)	0 [d]	257—260
$[ReCl_2(NCH_2)(py)(PMePh_2)_2]$	*trans*-P	Green		50.5 (50.3)	4.6 (4.4)	3.9 (3.7)	8.8 (9.3)	0 [d]	151—152
$[ReCl_2(NCH_2)(py)(PEtPh_2)_2]$	*trans*-P	Green	800 (793) [g]	51.4 (51.5)	4.7 (4.7)	3.3 (3.5)	9.2 (8.9)	0 [d]	196—198
$[ReCl_2(NCH_2)(py)(PPh_3)_2]$	*trans*-P	Green		56.4 (56.7)	4.4 (4.2)	3.3 (3.1)	8.5 (8.0)	0 [d]	210—212
$[ReCl_2(NCH_2)(PMe_2Ph)_3]$	*mer*-P	Grey-green		43.1 (42.9)	5.2 (5.0)	2.1 (2.0)	10.2 (10.2)	0 [d]	166—168
$[ReCl_2(NCHMe)(py)(PPh_3)_2]$	*trans*-P	Green		56.8 (57.2)	4.5 (4.4)	3.2 (3.1)	8.4 (7.9)		156—157 (decomp) [f]
$[ReCl_2(NCHEt)(py)(PPh_3)_2]$	*trans*-P	Green		57.2 (57.6)	4.7 (4.5)	3.3 (3.1)	8.2 (7.7)		*ca.* 148 (decomp.) [f]

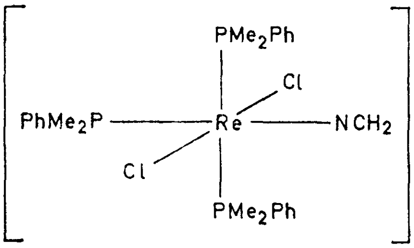
[a] Calculated values are given in parentheses. [b] Osmometric, in 1,2-dichloroethane. [c] Diamagnetic in the solid state. [d] In nitromethane. [e] In dichloromethane. [f] Determined in air. [g] Osmometric in benzene.

A member of another group of methyleneamido-complexes was obtained by using triethylamine in benzene as a dehydrohalogenating agent in the presence of an excess of the appropriate phosphine [reaction (1)]. This reaction could probably be extended to give a variety of products using different ligands to take the place of the abstracted chlorine atom. Imido-complexes

$$[ReCl_3(NMe)(PMe_2Ph)_2] + NEt_3 + PMe_2Ph \longrightarrow [ReCl_2(NCH_2)(PMe_2Ph)_3] \quad (1)$$

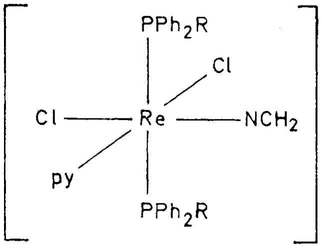
with no hydrogen atom on the α-carbon atom cannot give rise to methyleneamido-derivatives. Thus *trans*-$[ReCl_3(NPh)(PPh_3)_2]$ did not react with pyridine at room temperature, and under reflux the triphenylphosphine was replaced, to yield $[ReCl_3(NPh)(py)_2]$.

All the methylimido-complexes have a band in the region of 1 090 cm^{-1}, assigned to ν(Re=N), and also a band at *ca.* 1 315 cm^{-1} which is apparently characteristic of the NMe group. On conversion into the methyleneamido-complexes, these bands disappeared, but a new band was found at 1 560—1 590 cm^{-1}, which may be ν(C=N). In their ^{1}H n.m.r. spectra the methylimido-complexes each have a triplet in the region τ 9.2—9.8 due to NMe. On dehydrohalogenation this disappeared and was replaced by a resonance at τ *ca.* 11.2, assignable to the methylene protons. The configurations of the complexes are evident from the ^{1}H n.m.r. spectra. Thus, the CH$_3$ spectrum of $[ReCl_2(NCH_2)(PMe_2Ph)_3]$ indicates a *meridional* arrangement of phosphine ligands, and the methylene protons of the NCH$_2$ group give rise to two well separated triplets, consistent with the configuration (I). This accords with the far-i.r. spectrum which has a



(I)

single band only assignable to ν(Re–Cl). The configuration of $[ReCl_2(NCH_2)(py)(PPh_2R)_2]$ is different. The phosphorus atoms are mutually *trans*, according to the ^{1}H n.m.r., but the far-i.r. spectrum contains two bands assignable to ν(Re–Cl). These data suggest the configuration (II). In the complexes containing N=CHMe and N=CHEt, respectively, the unique hydrogen atom appears in the ^{1}H n.m.r. spectrum as a nonet and as a septet, and this, together with the two bands assignable to ν(Re–Cl), suggest that these complexes have the configuration (II) as inferred for the methyleneamido-complexes containing pyridine.



(II)

All the methyleneamido-derivatives react with hydrogen chloride to regenerate alkylimido-complexes, although in most cases these are ionic and not the parent complexes. However, in view of the reaction of the $N{=}CH_2$ group with protons, we investigated the reactions with alkylating agents. Ethyl bromide, even when present in a large excess, did not react with $[ReCl_2(NCH_2)(py)(PEtPh_2)_2]$. The addition of possible catalysts such as aluminium trichloride and $OEt_2{\cdot}BF_3$ to the alkylating reaction mixture yielded $[ReCl_2(NMe)(py)(PEtPh_2)_2]^+$ as the chloride and tetrafluoroborate, respectively. Evidently, trace amounts of water were also present. However, alkylation was achieved with methyl fluorosulphate on $[ReCl_2(NCH_2)(py)(PEtPh_2)_2]$ to yield $[ReCl_2(NEt)(py)(PEtPh_2)_2][SFO_3]$ which was fully characterised. Acetyl chloride in benzene reacted with $[ReCl_2(NCH_2)(py)(PEtPh_2)_2]$ to give *N*-acetylpyridinium chloride and a dark green, very air-sensitive, solid which could not be characterised but which reacted further with hydrogen chloride to produce *trans*-$[ReCl_3(NMe)(PEtPh_2)_2]$. The dark green solid is possibly $[ReCl_2(NCH_2)(PEtPh_2)_2]$. The reaction of propionyl chloride and $[ReCl_2(NCH_2)(PMe_2Ph)_3]$ produced no evidence of acylation and the only product obtained, after prolonged reaction, was $[ReCl_2(NMe)(PMe_2Ph)_3]Cl$ in poor yield. Thus, although it is possible to attack the NCH_2 group with electrophiles other than H^+, this is not easy.

Our results suggest that the ligand $N{=}CH_2$, like NO, NNH, NNR, and the comparable ligands CO and N_2, is susceptible to attack by electrophiles. We do not suggest that there is any necessary structure–reactivity correlation, but $N{=}CH_2$ like NO can probably act as either a three-electron or a one-electron donor with corresponding 'linear' and 'bent' structures and it is worthwhile enquiring whether the spectroscopic properties of the $N{=}CH_2$ group allow us to make a distinction between the two forms.

The inert-gas rule requires that NCH_2 in our rhenium complexes is a three-electron donor with a linear M–N–C system. In the i.r. spectra, ν(N=C) is found at *ca.* 1 560—1 590 cm^{-1}. The ^{1}H n.m.r. resonances of the methylene protons are at higher field than would be expected on the basis of unsaturation and proximity of the nitrogen atom, both of which would be expected to induce low-field shifts. Conjugation to the metal atom probably provides sufficient shielding to account for the observed high-field shifts. Nevertheless a spin-correlation effect cannot be excluded.

There are no closely similar methyleneamido-complexes for comparison, but in 'linear' $[Mo(\eta\text{-}C_5H_5)(CO)_2(N{=}CBu^tPh)]$, where the $N{=}CR_2$ ligand should be a three-electron donor,[1,6] ν(N=C) occurs in the range 1 615—1 660 cm^{-1}. However, its position changes considerably (to 1 550 cm^{-1}) if one CO is replaced by the better donor PPh_3, indicating a high sensitivity of ν(N=C) to the degree of back donation. The chemical shifts of the methyl groups of the t-butyl are generally *ca.* τ 8.5, which is not an unusual value for a methyl group, and our nearest comparison, the methyl of the propyleneamido-group in $[RCl_2(NCHEt)(py)(PPh_3)_2]$, is found at τ 9.12. This gives us little ground for inference.

The $N{=}CR_2$ group is also found in Main-group metal derivatives where it is unequivocally a one-electron donor and the M–N–C chain is presumably bent. For example, in $[GeBr_3(N{=}CBu^t{}_2)]$[2] ν(N=C) is at 1 624 cm^{-1} and the resonance of the methyl groups is at τ 8.81, rather similar to the resonance noted above. It seems unlikely that ^{1}H n.m.r. and i.r. data will allow a distinction to be made between bent and straight forms of the methyleneamido-ligand, just as the value of ν(NO) is not definitely diagnostic for bent or straight forms of M–N–O.

EXPERIMENTAL

All the reactions were carried out under an atmosphere of pure dry dinitrogen using solvents dried by standard procedures.

I.r. spectra (400—4 000 cm^{-1}) were recorded on a Unicam SP 1200 and on Perkin-Elmer 457 and 557 spectrometers. Far-i.r. spectra (40—400 cm^{-1}) were recorded in Polythene disks on an R.I.I.C. FS-620 interferometer. Magnetic moments were measured on a Faraday balance calibrated against cobalt mercury tetrathiocyanate, and conductivities were determined on a Portland Electronics series 300 conductivity bridge. Molecular weights were recorded on a Perkin-Elmer–Hitachi osmometer, and melting points were determined in sealed tubes at a pressure of *ca.* 0.1 mmHg * and are uncorrected. Hydrogen-1 n.m.r. spectra were recorded on Varian A60, T60, and HA100 instruments, using tetramethylsilane as an internal standard.

Trichlorobis(ethyldiphenylphosphine)(methylimido)-rhenium(V) and trichloro(n-propylimido)bis(triphenylphosphine)rhenium(V) were prepared by the literature method.[4] *trans*-Trichloro(methylimido)bis(triphenylphosphine)rhen-

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[6] H. M. M. Shearer and J. D. Sowerby, *J.C.S. Dalton*, 1973, 2629.

ium(v) (1) was prepared as in ref. 4, except that a three-fold excess of hydrazine dihydrochloride was used and it was necessary to employ benzene–acetone (1 : 1) as solvent. *trans*-Trichloro(phenylimido)bis(triphenylphosphine)rhenium(v) (3) was also prepared according to ref. 4, but using 1-acetyl-2-phenylhydrazine. Care was necessary when reducing the volume of the resulting brown-green solution because at low volumes some grey-red crystals were precipitated together with the desired product.

trans-Trichloro(ethylimido)bis(triphenylphosphine)rhenium(v) (2) was prepared according to ref. 4. A better recipe is as follows. Trichloro-oxobis(triphenylphosphine)rhenium(v)[7] (0.50 g, 1 mol), 1,2-diethylhydrazine (0.75 g, 15 mol), and triphenylphosphine (0.50 g, 3.2 mol) were heated under reflux in acetone (50 cm^3) for 3 h. A greenish blue microcrystalline *complex* was produced on standing at room temperature overnight. It was filtered off and recrystallised from dichloromethane.

trans-*Bis(allyldiphenylphosphine)trichloro(methylimido)rhenium*(v).—A suspension of (1) (0.70 g, 1 mol) in benzene (35 cm^3) and allyldiphenylphosphine (1.81 g, 8 mol) were heated under reflux for 10 min. The resulting blue solution was cooled, filtered, and evaporated to *ca.* 15 cm^3, and the *complex* was precipitated as a blue solid by the addition of ethanol (60 cm^3). The product was recrystallised from dichloromethane.

trans-*Trichlorobis[(methylallyl)diphenylphosphine](methylimido)rhenium*(v).—A suspension of (1) (0.79 g) in benzene (35 cm^3) and (methylallyl)diphenylphosphine (1.73 g) were heated under reflux for *ca.* 20 min. The resulting blue solution was cooled, filtered, and the filtrate evaporated to about a quarter of its bulk. The *complex* was precipitated by the addition of ethanol (80 cm^3) as a blue solid which was recrystallised as blue prisms from dichloromethane.

cis- *and* trans-*Trichlorobis(dimethylphenylphosphine)(methylimido)rhenium*(v).—A suspension of (1) (1.6 g, 1 mol) in benzene (50 cm^3) and dimethylphenylphosphine (1.8 g, 10 mol) were brought just to boiling. Subsequent cooling of the resulting blue solution yielded the *cis* isomer as a violet microcrystalline precipitate which was filtered off and recrystallised as violet needles from dichloromethane (0.34 g, 30%). The blue filtrate was evaporated to about a quarter of its bulk and the *trans* isomer was precipitated by the addition of light petroleum (b.p. <40 °C) and recrystallised as blue prisms from dichloromethane (0.52 g, 46%).

cis- *and* trans-*Trichlorobis(methyldiphenylphosphine)(methylimido)rhenium*(v).—A suspension of (1) (2.1 g, 1 mol) in benzene (75 cm^3) and methyldiphenylphosphine (5.02 g) were brought just to boiling. Subsequent cooling of the resulting blue solution yielded the *cis* isomer as a violet microcrystalline precipitate which was filtered off and recrystallised from dichloromethane (0.61 g, 34%). The blue filtrate was evaporated to about half its bulk and the *trans* isomer was precipitated by the addition of light petroleum (b.p. <40 °C) and recrystallised as blue prisms from dichloromethane (0.86 g, 48%).

trans-*Trichloro(ethylimido)bis(methyldiphenylphosphine)rhenium*(v).—A suspension of (3) (0.50 g, 1 mol) and $PMePh_2$ (1.22 g) were heated under reflux in benzene (25 cm^3) for *ca.* 5 min. The resulting blue solution was evaporated to about a quarter of its bulk and the *complex* was precipitated as a dark blue solid by the addition of methanol (30 cm^3). The product was recrystallised from dichloromethane as dark blue prisms.

Dichlorobis(ethyldiphenylphosphine)(methylimido)pyridinerhenium(v) *Chloride*.—To a solution of dichlorobis(ethyldiphenylphosphine)(methyleneamido)(pyridine)rhenium(iii) (0.1 g) in benzene (3 cm^3) was added a large excess of concentrated hydrochloric acid (0.05 cm^3). Within 1 min a purple solution was formed from which the *complex* slowly precipitated as a violet solid which was filtered off and recrystallised from dichloromethane–diethyl ether (0.76 g, 73%). Addition of diethyl ether to the filtrate afforded the neutral complex, *trans*-$[ReCl_3(NMe)(PEtPh_2)_2]$, identified by comparison with an authentic sample (0.01 g, 10%).

Dichlorobis(ethyldiphenylphosphine)(methylimido)pyridinerhenium(v) *Tetrafluoroborate*.—A solution of $[ReCl_2(NCH_2)(py)(PEtPh_2)_2]$ (0.2 g) was stirred in ethyl bromide (10 cm^3) for 18 h. No reaction occurred. Then $OEt_2{\cdot}BF_3$ (0.02 cm^3) was added. A purple solution formed immediately, from which a violet solid slowly precipitated. The *product* was filtered off, recrystallised from dichloromethane–diethyl ether, and characterised as $[ReCl_2(NMe)(py)(PEtPh_2)_2][BF_4]$ (0.14 g, 63%).

Dichlorotris(dimethylphenylphosphine)(methylimido)rhenium (v) *Chloride*.—Dichlorotris(dimethylphenylphosphine)methyleneamidorhenium(iii) (0.2 g) was treated with propionyl chloride (0.44 cm^3, 15 mol) in benzene (10 cm^3). No acylation occurred, and over a period of 80 h a small amount of pink precipitate formed; the *product* was filtered off and recrystallised from dichloromethane (0.04 g, 19%). The formation of the product was probably due to adventitious moisture.

Dichlorobis(ethyldiphenylphosphine)(ethylimido)pyridinerhenium(v) *Fluorosulphate*.—To a solution of $[ReCl_2(NCH_2)(py)(PEtPh_2)_2]$ (0.1 g) in benzene (2 cm^3) was added methyl fluorosulphate (0.6 cm^3, 60 mol). After stirring at room temperature for 1 h, a purple solution was formed which was evaporated to dryness under reduced pressure. The *complex* was recrystallised from benzene–hexane as a violet microcrystalline solid (0.71 g, 62%).

trans-*Bis(allyldiphenylphosphine)trichloro(phenylimido)rhenium*(v).—A suspension of (2) (0.91 g, 1 mol) in benzene (35 cm^3) and allyldiphenylphosphine (1.95 g, 8.5 mol) were heated under reflux for 10 min. The resulting clear green solution was cooled, evaporated to *ca.* 15 cm^3, and the *complex* was precipitated by the addition of ethanol (60 cm^3) as a green solid which was recrystallised from dichloromethane.

Trichloro(phenylimido)bis(pyridine)rhenium(v).—*trans*-Trichloro(phenylimido)bis(triphenylphosphine)rhenium(v) (0.50 g) and pyridine (15 cm^3) were heated under reflux for 3 h and the resulting green solution was evaporated to about a quarter of its bulk yielding a green powder. After refrigeration at 0 °C overnight, the powder was filtered off and recrystallised as green platelets from dichloromethane.

Dichlorobis(methyldiphenylphosphine)(methyleneamido)pyridinerhenium(iii).—Pyridine (20 cm^3) and *cis*-trichlorobis(methyldiphenylphosphine)(methylimido)rhenium(v) (0.5 g) were stirred at room temperature for *ca.* 100 h and the resulting dark green solution was evaporated to about a quarter of its bulk. After filtering, diethyl ether (50 cm^3) was added slowly to the filtrate to precipitate the *complex* as a green microcrystalline solid. The latter was filtered off, washed with diethyl ether, and dried at 0.1 mmHg and 100 °C (0.33 g, 62%). The same product may be obtained starting from *trans*-trichlorobis(methyldiphenylphosphine)(methylimido)rhenium(v).

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[7] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019.

Dichlorobis(ethyldiphenylphosphine)(methyleneamido)rhenium(III).—Pyridine (30 cm^3) and *trans*-trichlorobis(ethyldiphenylphosphine)(methylimido)rhenium(V) (0.75 g) were stirred at room temperature for *ca.* 72 h and the resulting green solution was evaporated to about a fifth of its bulk. After filtering, diethyl ether (45 cm^3) was added slowly to the filtrate yielding a green *complex* which was filtered off, washed with diethyl ether (3 × 10 cm^3), and dried at 0.1 mmHg and 100 °C (0.52 g, 66%). A white sublimate of pyridine hydrochloride was also obtained during the drying procedure.

Dichloro(methyleneamido)pyridinebis(triphenylphosphine)rhenium(III).—Pyridine (40 cm^3) and (1) (0.50 g) were stirred at room temperature for *ca.* 18 h and the resulting green solution evaporated to about a third of its bulk. After filtering, diethyl ether (40 cm^3) was added slowly to the filtrate yielding the green *complex*, which was filtered off, washed with diethyl ether (3 × 10 cm^3), and dried at 0.1 mmHg and 100 °C (0.36 g, 68%). A white crystalline product sublimed on to the walls of the drying pistol. This was later identified as pyridine hydrochloride.

Dichlorotris(dimethylphenylphosphine)(methyleneamido)rhenium(III).—Triethylamine (10 cm^3), dimethylphenylphosphine (1.39 g), and *trans*-trichlorobis(dimethylphenylphosphine)(methylimido)rhenium(V) (0.50 g) were heated under reflux for *ca.* 5 h in benzene (5 cm^3) and the reaction mixture left overnight at room temperature. The resulting green crystalline *complex* was filtered off and washed with diethyl ether (3 × 5 cm^3) and then degassed water until tests for Cl$^-$ in the filtrate were negative. After further washing with diethyl ether the dark green crystals were dried at 0.1 mmHg and 100 °C (0.35 g, 63%).

Dichloro(methylmethyleneamido)pyridinebis(triphenylphosphine)rhenium(III).— Trichloro(ethylimido)bis(triphenylphosphine)rhenium(V) (0.2 g) was suspended in benzene (5 cm^3); sufficient pyridine was added just to dissolve the starting material (*ca.* 20 cm^3). The solution was stirred at room temperature for 45 min and then evaporated to 7 cm^3 at 0.1 mmHg. Careful addition of diethyl ether (10 cm^3) to the solution precipitated the *complex* as a green microcrystalline solid which was filtered off, and washed with water (3 × 5 cm^3), methanol (1 × 5 cm^3), and diethyl ether (2 × 10 cm^3) (0.1 g, 48%).

Dichloro(ethylmethyleneamido)pyridinebis(triphenylphosphine)rhenium(III).—This complex was prepared similarly to the corresponding methylmethyleneamido-complex, using trichloro(n-propylimido)bis(triphenylphosphine)rhenium(V) (0.2 g). The *complex* was isolated as a green microcrystalline solid (0.12 g, 57%).

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