



STUDIES ON THE OXIDATION REACTIONS OF THE DINITROGEN COMPLEX *trans*- -[ReCl(N₂)(Ph₂PCH₂CH₂PPh₂)₂]

Complex *trans*-[ReCl(N₂)(dppe)₂] (A, dppe = Ph₂PCH₂CH₂PPh₂) undergoes oxidation by AgBF₄ to give the derived analogous cationic species with a labile N₂ ligand which undergoes ready replacement by CNMe to afford *trans*-[ReCl(CNMe)(dppe)₂][BF₄]; alternatively, a rearrangement of the unsaturated [ReCl(dppe)₂][BF₄] complex appears to afford an ortho-metalated species. Photochemical chlorination of A by CH₂Cl₂ gives [Re₂Cl₃(dppe)₄], whereas the oxo compound [ReOCl(dppe)₂] is formed in the presence of dioxygen; photolysis of a solution of A in the absence of any substrate affords the possible dimeric ortho-metalated complex [Re₂Cl₂(dppe)₃].

1 — INTRODUCTION

Electron-rich dinitrogen complexes are easily oxidizable species and their oxidations generally result in dinitrogen evolution [1] in agreement [2] with expectations based upon some simplified π -MO schemes. However, in some cases where the metal-dinitrogen bond is strong enough, e.g., in *trans*-[ReCl(N₂)(dppe)₂], A, a stable mono-oxidized species with bonded N₂ may be formed upon oxidation of the parent complex [3]; nevertheless, a weakening of the N-N₂ bond is expected [2] to result from the metal oxidation, and this behaviour was tested in the present work by studying the reaction of *trans*-[ReCl(N₂)(dppe)₂]⁺ with isocyanide.

The evolution of the dinitrogen ligand may also result from photochemical excitation and the unsaturated complex [ReCl(dppe)₂], with a trigonal bipyramidal structure, was isolated from a toluene solution of complex A, under tungsten filament light [4]. In the present work we looked for other products of this reaction, also in the absence of any substrate but under stronger irradiation conditions; moreover, the behaviour of the unsaturated centre, generated *in situ*, in the presence of an oxidizing agent (dichloromethane or dioxygen) was also the object of this study.

2 — RESULTS AND DISCUSSION

2.1 — Oxidation of *trans*-[ReCl(N₂)(dppe)₂], A, by Ag⁺ followed by reaction with CNMe or by rearrangement of the metal centre

Complex A undergoes oxidation by AgBF₄ in thf to afford the cationic species *trans*-[ReCl(N₂)(dppe)₂][BF₄], B, as very dark green or purple platelets, with i. r. ν (N₂) at 2030 cm⁻¹, in agreement with studies quoted by other authors [3]; the observed differen-

ces in colour may correspond to different dppe distortional isomers since differences in their infrared spectra were detected in the 600-800 cm^{-1} phenyl region.

The higher i.r. $\nu(\text{N}_2)$ value (2030 cm^{-1}) observed for complex B, compared to the value (1960 cm^{-1}) shown by compound A, suggests a weaker Re- N_2 bond for the former. Since

Table 1

Physical data for complexes $\text{trans-[ReCl(N}_2\text{)(dppe)}_2\text{][BF}_4\text{]}$ (B), $\text{trans-[ReCl(CNMe)(dppe)}_2\text{][BF}_4\text{]}$ (C), $[\text{ReCl(dppe)}_2\text{][BF}_4\text{]}$ (D, ortho-metalated), $[\text{ReCl(dppe)}_2]_2(\mu\text{-Cl})$ (E), $[\text{ReOCl(dppe)}_2]$ (F) and $[\text{ReCl}_2(\text{dppe})_3]$ (G, ortho-metalated)

Complex	Colour	Elemental microanalysis ^a			Relevant i.r. data ^b	Δ_M^c	μ_{eff} B.M.	Molecular weight ^{a,d}
		% C	% H	% N				
B	Very dark red/green	55.3(55.1)	4.6(4.3)	2.9(2.5)	2030m[$\nu(\text{N}_2)$] 1050vs(BF_4^-)	80	1.9	—
C	Red	56.9(56.6)	5.0(4.5)	1.0(1.2)	2070s[$\nu(\text{CN})$] 1050vs(BF_4^-)	80	1.8	—
D	Yellow	56.1(56.5)	4.5(4.4)	—	1585sh, 1570m 1555m, 1525sh 1050vs(BF_4^-) 340ms[$\nu(\text{ReCl})$] ^e	70	3.95	$1.0 \times 10^3(1105.3)$
E	Yellow	60.2(60.3)	4.9(4.7)	—	280wm[$\nu(\text{ReCl})$]	^f	1.8	$1.94 \times 10^3(2072.4)$
F	Rose	49.4(49.1)	4.0(3.8)	—	903s[$\nu(\text{Re} = \text{O})$]	^g	^h	$1.03 \times 10^3(1034.5)$
G	Pink	57.6(57.3)	4.6(4.4)	—	785m ^e	^g	^h	$1.59 \times 10^3(1638.5)$

^a Required values in parentheses. ^b In Nujol null. ^c In $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, measured in nitromethane, unless stated otherwise. ^d Measured in 1,2-dichloroethane. ^e Associated to ortho-metalated phosphine. ^f Non-electrolyte in nitromethane solution. ^g Non-electrolyte in 1,2-dichloroethane solution. ^h Diamagnetic.

complex B (Table 1) is paramagnetic ($\mu_{\text{eff}} = 1.9 \text{ B. M.}$ in accordance with the presence of one unpaired electron), 1:1 electrolyte in nitromethane ($\Delta_M = 80 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and a singlet due to the BF_4^- anion is observed in the ^{19}F n.m.r. spectrum. No ^{31}P n.m.r. was observed, possibly due to the paramagnetism, and the ^1H n.m.r. spectrum displays very unusual sharp multiplet patterns along a wide range (Table 2) due to paramagnetic contact shifts.

the Re- N_2 bond in complex A presents a remarkable strength and, e.g., the replacement of dinitrogen by CNMe in a considerable extension requires a long refluxing time (above one week with partial decomposition) in thf, under argon, it would be advantageous to find a way to accelerate the loss of N_2 from the rhenium centre in order that the dinitrogen complex could be applied as a much more convenient starting material for the preparation of other

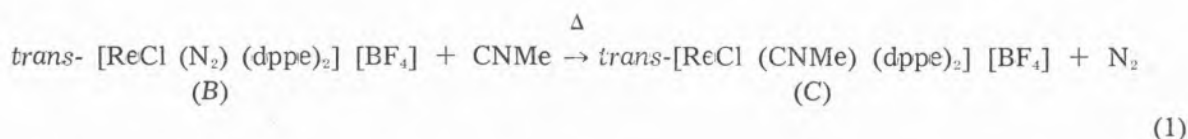
Table 2

^1H and ^{31}P n.m.r. data ^a for complexes $\text{trans-}[\text{ReCl}(\text{N}_2)(\text{dppe})_2][\text{BF}_4]$ (B), $\text{trans-}[\text{ReCl}(\text{CNMe})(\text{dppe})_2][\text{BF}_4]$ (C), $[\text{ReCl}(\text{dppe})_2][\text{BF}_4]$ (D, ortho-metalated), $[\{\text{ReCl}(\text{dppe})_2\}(\mu\text{-Cl})]$ (E), $[\text{ReOCl}(\text{dppe})_2]$ (F) and $[\text{Re}_2\text{Cl}_2(\text{dppe})_3]$ (G, ortho-metalated).

Complex	δ (^1H) ppm	Integration	Assignment
B	9.56 s,br	2	C_6H_5 (dppe)
	9.11 t b	2	
	8.05 t b	4	
	7.34 s	3	
	ca. 7.34-5.9 m,br c	29	CH_2 (dppe)
	2.11 s	2	
	1.25 s	4	
	-4.55 d b	2.5	
C	16.28 d d	3	C_6H_5 (dppe)
	16.15 d d	3	
	10.16 br	1.5	
	9.57 s	2	
	9.42 d b	2	
	9.13 t b	2	
	8.47 t b	3	
	8.08 t b	3	CH_2 (dppe) + CNCH_3
	7.82 d b	1	
	7.34-7.08 m	19.5	
	5.6 m,br	3	
	2.85 s	2	
	2.42 t d	3	
D	16.33 d f	2	$\text{C}_6\text{H}_5 + o\text{-C}_6\text{H}_4$ (dppe)
	16.19 d f	5	
	ca. 10.2 m,br	3	
	9.59 d g	2	
	9.44 d h	4	
	9.15 t b	2	
	8.50 t b	6	CH_2 (dppe)
	8.10 t b	3	
	7.97 s	1	
	7.84 d h	3	
	7.33 s,br	8	
	5.6 d,br h	6	
	ca. 3.2-2.3 m,br	1	CH_2 (dppe)
	1.57 s	1	
E	ca. 13.5-6.0 m,br	80	C_5H_5 (dppe)
	ca. 4.5-1.0 m,br	16	CH_2 (dppe)
F i	8.4-6.6 m	40	C_6H_5 (dppe)
	3.4-1.2 m,br	8	CH_2 (dppe)
G j	8.3-7.9 m	8	$o\text{-C}_6\text{H}_4$ (dppe)
	7.8-6.9 m	50	C_6H_5 (dppe)
	3.0-1.9 m,br	12	CH_2 (dppe)
	-2.2 br	ca. 2	Hydrides

^a In CD_2Cl_2 solution. δ (^1H) relative to internal TMS. δ (^{31}P) relative to external TMP. b $J = 7.3\text{Hz}$. c Four broad resonances centered at δ ca. 7.3, 6.9 6.45 and 6.15 ppm. d $J = 8.2\text{Hz}$. e No further resonances were observed up to $\delta = -15.7\text{ ppm}$. f $J = 8.0\text{Hz}$. g $J = 4.6\text{Hz}$. h $J = 6.8\text{Hz}$. i δ (^{31}P) = -130s (ppm) . j δ (^{31}P) = -106.9 d (43.2Hz) , -125.6 s , -129.6 s , -137.3 s , $-147.6\text{ d (43.2 Hz)}$, $-159.4\text{ d (43.2Hz) (ppm)}$.

complexes with related ligands (such as, isocyanides, carbonyl, nitriles, acetylenes, etc). Hence, the reaction of complex *B* with CNMe (ca. 3 molar excess) was studied in thf and, upon only 3h reflux under N_2 , a red compound, *C*, could be isolated which, on the basis of microanalytical, i.r., magnetic, molar conductivity and 1H n.m.r. data (Tables 1 and 2), is formulated as the expected isocyanide complex *trans*-[ReCl (CNMe) (dppe) $_2$] [BF $_4$], obtained through replacement of N_2 by CNMe (equation 1).



Complex *C* exhibits, in the i.r. spectrum, a strong band at 2070 cm^{-1} assigned to $\nu(CN)$ (much higher than that observed in the neutral *trans*-[ReCl (CNMe) (dppe) $_2$] at ca. $1800\text{--}1830\text{ cm}^{-1}$) and a very strong one at ca. 1050 cm^{-1} associated to the BF_4^- counterion; the i.r. data agree with those observed for another sample of complex *C* which was prepared independently by oxidation of the parent neutral isocyanide compound [5]. Compound *C* is paramagnetic ($\mu_{eff} = 1.8\text{ B.M.}$ in agreement with a $d^5\text{ Re}^{II}$ octahedral centre) and a 1:1 electrolyte in nitromethane ($\Lambda_M = 85\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$); its 1H n.m.r. spectrum exhibits unusual complex sets of sharp multiplets spread over a wide range (Table 2) and no resonance was found in the ^{31}P n.m.r. spectrum, as it was observed in the related paramagnetic complex *B*.

The reaction of the oxidized dinitrogen complex *B* with CNMe in refluxing thf was described above.

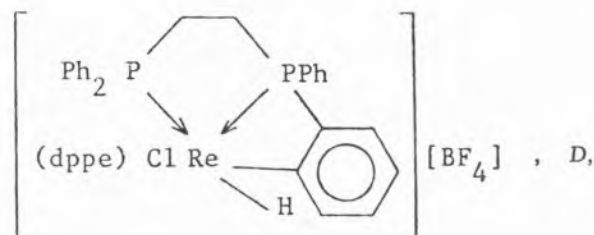
However, another, species, *D*, yellow in colour is also isolated from the reaction mixture as well as from a simple refluxing thf solution of complex *B*, in the absence of isocyanide.

No bands assignable to $\nu(NN)$ or $\nu(CN)$ are observed in the i.r. spectrum of *D* which only exhibits, as main bands and apart from those

due to dppe, a very strong one at 1050 cm^{-1} (BF_4^-) and a medium/strong band at 340 cm^{-1} which may conceivably be assigned to $\nu(Re-Cl)$. Microanalytical, molar conductivity ($\Lambda_M = 70\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ in nitromethane) and molecular weight (1.0×10^3 compared to the expected value, 1105.3) data (Table 1) agree with the formulation [ReCl (dppe) $_2$] [BF $_4$] for species *D*. However, such a formulation would correspond to a 15-electron complex and it would be unacceptable particularly in the strong isocyanide ligand.

Complex *D*, however, presents a high paramagnetism ($\mu_{eff} = 3.95\text{ B.M.}$ which correspond to three unpaired electrons), its 1H n.m.r. spectrum consists of a series of sharp multiplets spread over a wide range (Table 2) and its i.r. spectrum exhibits, in the region just below 1600 cm^{-1} , a complex pattern which may be diagnostic [6] of an *ortho*-metalated phosphine ligand: 1585 sh, 1570 m, 1555 m and 1525 sh, whereas, in the absence of *ortho*-metalation, only two bands would be expected, as it is usually observed in other dppe complexes.

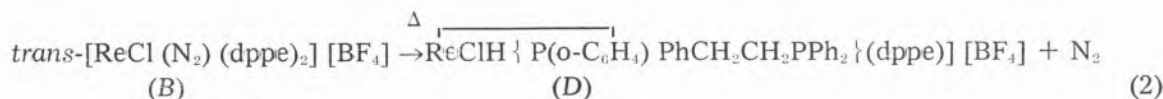
Hence, species *D* is tentatively formulated as an *ortho*-metalated compound of the type



with Re (IV), d^3 , in agreement with the paramagnetic properties; it is a 17-electron complex which is coordinatively saturated (the coordination number is seven) which accounts

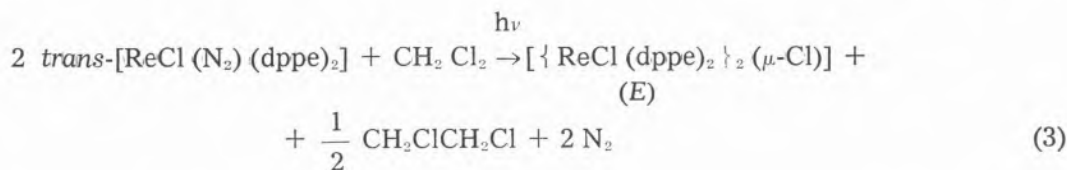
for its stability towards the addition of an isocyanide ligand

Complex *E* appears to be formed according to overall reaction (3) where the dichlorome-



Hence, one may possibly conclude that the dinitrogen ligand in the oxidized *trans*-[ReCl(N₂)(dppe)₂]⁺ complex presents a considerable lability and, upon heating, it is evolved to generate an unsaturated 15-elec-

thane, under irradiation, behaves as a chlorinating agent (giving possibly 1,2-dichloroethane) of the {ReCl(dppe)₂} centre to afford a mixed valence Re(I)/Re(II) dimeric species. Hence, dichloromethane is able to oxi-



tron centre which may bind another substrate (such as an isocyanide, reaction 1) or, alternatively may rearrange through an *ortho*-metalation (undergoing a phenyl C-H bond oxidative addition, reaction 2) to afford a different saturated complex.

dize that electron-rich centre, although presenting, as expected, a milder oxidizing power than chlorine since the dichlorocomplex of Re(III), [ReCl₂(dppe)₂]Cl, is the product [3] of the reaction of the dinitrogen complex *A* with an excess of chlorine in chloroform.

2.2 — Reaction of *trans*-[ReCl(N₂)(dppe)₂], *A*, with dichloromethane

If a benzene solution of complex *A* with dichloromethane is irradiated with tungsten-filament light for ca. 2 days, a yellow species, *E*, may be isolated; it is formulated as the dimeric compound (possibly with a bridging chloro ligand) [{ReCl(dppe)₂}]₂(μ-Cl), on the basis of microanalytical, molecular weight (1.94 × 10³ in 1,2-dichloroethane, compared to the expected value of 2072.4), magnetic susceptibility (μ_{eff} ≈ 1.8BM, which corresponds to one unpaired electron per two metal atoms), molar conductivity (non-electrolyte in nitromethane) and infrared data [a weak/medium band at 280 cm⁻¹ is assigned to ν(ReCl)] (Table 1). On account of the paramagnetism, the ¹H n.m.r. spectrum of *E* exhibits very broad resonances for the phenyl and the methylene protons (Table 2).

2.3 — Reaction of *trans*-[ReCl(N₂)(dppe)₂], *A*, with dioxygen and photolysis in the absence of any substrate.

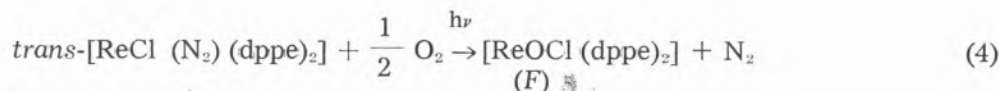
In the previous section the photochemical reaction of complex *A* with CH₂Cl₂ in benzene (toluene) was mentioned. However, in the absence of CH₂Cl₂ but in the presence of traces of air, a different oxidized species, *F*, is isolated, being formulated as the oxo complex [ReOCl(dppe)₂], possibly formed according to equation (4).

It is rose in colour, a strong i.r. band observed at 903 cm⁻¹ is assigned to ν(Re=O), its molecular weight in 1,2-dichloroethane (1.03 × 10³) agrees with the expected value (1034.5) and it is a non-electrolyte in this solvent.

Complex *F* is diamagnetic and its ¹H and ³¹P n.m.r. spectra (Table 2) agree with the

proposed formulation. It is also a product of the deoxygenation reaction of carbon dioxide

In the ^1H n.m.r. spectrum (Table 2), a broad resonance (which integrates for 2H^+) is



by complex A, which will be described separately.

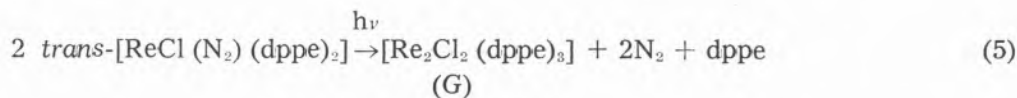
If the photolysis of a toluene solution of complex A (under one 100 Watt tungsten filament bulb) is carried out in the *absence* of any substrate, the unsaturated complex $[\text{ReCl}(\text{dppe})_2]$, whose structure was authenticated by X-rays, was isolated [4].

However, under stronger irradiation conditions [e.g., by using four 100 Watt tungsten filament bulbs at a short distance from the toluene reaction solution or by irradiating a thf solution of complex A with two 150 watt tungsten filament bulbs for an extended period of 5 days] the reaction appears to proceed with liberation of phosphine to afford a pink species formulated as $[\text{Re}_2\text{Cl}_2(\text{dppe})_3]$, G, (reaction 5) mainly on account of microanalytical data, molecular weight measurements (1.59×10^3 in 1,2-dichloroethane, compared to the expected value of 1638.5) and conductivity data (it is a non-electrolyte in this

observed at high field ($\delta = -2.2$ ppm) whereas a complex multiplet (which integrates for 8H^+) occurs at low field ($\delta = 8.3 - 7.9$ ppm), below the usual phenyl proton range; these resonances may be assigned [7] to the hydride ligands and to the aromatic $o\text{-C}_6\text{H}_4$ groups involved in the *ortho*-metalation. Moreover, although the i.r. region just below 1600 cm^{-1} is not clear enough, extra bands with a high intensity are observed at 785 cm^{-1} (sharp), 1095 cm^{-1} (broad) and 1190 cm^{-1} and, at least the first two of them, have been assigned [7,8] to a phenyl group involved in *ortho*-metalation.

The ^{31}P n.m.r. spectrum of compound G is a complex multiplet (Table 2) which spans over a wide range, as expected in view of the presence of different types of phosphorus nuclei involved in chelate rings of distinct sizes.

The lowest field ^{31}P resonance occurs at a chemical shift [$\delta = -106.9$ ppm relative to



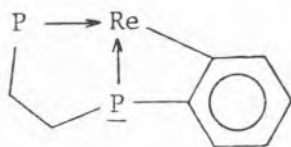
solvent) (Table 1). The dimeric structure would result from chloro or/and dppe bridges between the two metal centres.

However, this simple formulation of species G would correspond to a highly unsaturated metal site unless, as it was suggested for complex D, an *ortho*-metalation is postulated to occur. Moreover, this proposal is substantiated by some n.m.r. and i.r. data as follows.

$\text{P}(\text{OMe})_3$ which is similar to those observed for chelating dppe ligands in related complexes [e.g. -108.6 and -109.8 ppm for $\text{trans-}[\text{ReCl}(\text{CNMe})(\text{dppe})_2]$ [9] and $\text{trans-}[\text{ReCl}(\text{C}=\text{CHPh})(\text{dppe})_2]$, [10], respectively]; hence, it is associated to a phosphorus nucleus in a 5-membered ring of a chelating dppe ligand.

The chemical shift of the highest field ^{31}P resonance ($\delta = -159.4$ ppm) occurs 52.5 ppm

upfield from the abovementioned resonance, and this shift is identical to that expected (ca. 52 ppm) [11] for the contribution of a 4-membered ring which, in complex G, conceivably results from an *ortho*-metalation. Hence, the resonance at $\delta = -159.4$ ppm is tentatively assigned to a phosphorus atom of a chelating dppe ligand which is also involved in an *ortho*-metalation, i.e.,



The ³¹P n.m.r. spectrum also exhibits resonances which are intermediate between the abovementioned limits and, possibly, they may be associated, in part, to a non-chelating (bridging) dppe ligand whose phosphorus resonance would be expected [11] to occur at ca. 33 ppm upfield from that ($\delta = -106.9$ ppm) of the P atom in the chelating ligand.

3 — FINAL COMENTS

Chemical oxidation or photochemical excitation promotes the lability of N₂ at the *trans*-[ReCl(N₂)(dppe)₂] complex which can then undergo a ready replacement of the N₂ ligand by a non-oxidizing substrate (such as isocyanide) or which, upon N₂ loss, may be further oxidized by an oxidizing agent (e.g., being chlorinated by dichloromethane or oxygenated by dioxygen). In the absence of any substrate, dinitrogen evolution is followed by an internal oxidative-addition reaction (*ortho*-metalation) to afford coordinatively saturated oxidized species.

The easy oxidation of the electron-rich centre {ReCl(dppe)₂} and the ability of this unsaturated site to bind various substrates are well patent in the reactions described in this study.

4 — EXPERIMENTAL

All the reactions (unless otherwise stated) were carried out in the absence of air using standard inert gas flow and vacuum techniques. Solvents were purified by standard techniques and *trans*-[ReCl(N₂)(dppe)₂], A, was prepared by a published method [3]. Infrared measurements were carried out on a Perkin-Elmer 683 spectrometer ¹H and ³¹P n.m.r. spectra were recorded on a Jeol JNM-PS-100, a Bruker CXP 300 or a Jeol PFT 100 Fourier-transform spectrometer. Molecular weights and magnetic susceptibilities were determined using a Perkin-Elmer osmometer and a Faraday balance, respectively. Conductivities were measured using a Portland Electronics P 310 conductivity bridge.

— Preparation of *trans*-[ReCl(N₂)(dppe)₂] [BF₄], B

AgBF₄ (0.282 g) was added to a stirred solution of *trans*-[ReCl(N₂)(dppe)₂] (0.329 g) in thf (140 cm³). An immediate formation of a fine black precipitate of metal silver occurred, whereas the solution became very dark. After ca. 1h, the solution was filtered, concentrated under vacuum and a very dark purple (violet) solid precipitated out upon addition of pentane. This solid was filtered-off, washed with a mixture of thf/pentane and dried under vacuum; it was then recrystallised from CH₂Cl₂/Et₂O to afford complex B as very dark/violet platelets (ca. 0.3 g) which were filtered-off, washed with a mixture of CH₂Cl₂/Et₂O and dried under vacuum (very dark green was the final colour of the dried product).

— Preparation of *trans*-[ReCl(CNMe)(dppe)₂] [BF₄], C, and [ReCl(dppe)₂] [BF₄], D.

A solution of *trans*-[ReCl(N₂)(dppe)₂] [BF₄], B (0.309 g), with CNMe (0.15 ml, i.e., in a

3.2 molar excess) in thf (60 cm³) was refluxed under N₂ for ca. 3h; during this period the solution colour changed from dark violet to red. It was then concentrated under vacuum, with heating, until complex *D* precipitated as a yellow solid (ca. 0.090 g) which was filtered-off, washed with a mixture of thf/pentane dried under vacuum (the same compound may be prepared, in a better yield, by carrying out the reaction in the absence of CNMe and under identical experimental conditions).

The mother liquor solution (red in colour) separated from *D* by filtration was concentrated and complex *C* precipitated out (ca. 0.20 g) as a red solid upon addition of pentane; it was filtered-off, washed with a mixture of thf/pentane and dried under vacuum.

— Preparation of $[\{\text{ReCl}(\text{dppe})_2\}_2(\mu\text{-Cl})]$, *E*

A benzene (250 cm³) solution of *trans*-[ReCl(N₂)(dppe)₂], *A* (0.40 g), with CH₂Cl₂ (ca. 0.1 ml) was prepared under argon (this addition of CH₂Cl₂ may not be required provided that complex *A* was previously recrystallized from CH₂Cl₂: the solvent of crystallization is enough for the reaction to occur). The stirred solution was then irradiated, under reduced pressure, by two 100 Watt tungsten-filament bulbs for ca. 2 days. The reaction solution was then heated to dryness, under vacuum, and the resulting solid was washed with hot benzene. The yellow residue of complex *E* (ca. 0.15 g) was then dried under vacuum.

— Preparation of [ReOCl(dppe)₂], *F*

To a solution of complex *trans*-[ReCl(N₂)(dppe)₂] (0.35 g) in toluene (250 cm³), which was prepared under argon, a portion of air was admitted. The solution was then irradiated by four 100 Watt tungsten filament bulbs for about 2 days, concentrated, with heating, under vacuum, until complex *F* precipitated as a rose solid which was filtered-off,

washed with toluene and dried under vacuum. A further crop of species *F* could be obtained upon concentration of the mother liquor and addition of petroleum ether 40-60; the precipitate was washed with toluene and the residue (species *F*) was dried under vacuum (the total amount of *F* was ca. 0.10 g).

— Preparation of [Re₂Cl₂(dppe)₃], *G*

A stirred solution of *trans*-[ReCl(N₂)(dppe)₂], *A* (0.30 g), in toluene (200 cm³), which was prepared under argon, was irradiated by four 100 Watt tungsten filament bulbs for about 2 days. It was then concentrated under vacuum and pentane was added until a brownish solid precipitated out. The solution was filtered and a brownish pink solid was obtained upon addition of petroleum ether 40-60; this solid was filtered-off and recrystallized from hot toluene to afford complex *G* as a brownish pink solid which was filtered-off, washed with a mixture of toluene/petroleum ether and dried under vacuum (ca. 0.070 g).

Complex *G* may also be prepared by irradiating a thf solution (250 cm³) of compound *A* (0.20 g) with two 150 Watt tungsten filament bulbs for 5 days. The solution was then concentrated under vacuum and pentane was added until appearance of a yellowish solid which was filtered-off. The resulting solution was again concentrated and complex *G* precipitated as a pink solid upon addition of pentane; it was filtered-off, washed with a mixture of thf/pentane and dried under vacuum (ca. 0.060 g).

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RESUMO

Estudo de reacções de oxidação do complexo $\text{trans-[ReCl(N}_2\text{)(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{)]}$

A oxidação do complexo $\text{trans-[ReCl(N}_2\text{)(dppe)}_2\text{]}$ (A , $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) por AgBF_4 conduz à formação de uma espécie catiónica em que o ligando N_2 apresenta acentuada labilidade sendo facilmente substituído por CNMe formando $\text{trans-[ReCl(CNMe)(dppe)}_2\text{)][BF}_4\text{]}$; em alternativa, pode ocorrer um rearranjo do complexo insaturado $[\text{ReCl(dppe)}_2][\text{BF}_4]$ com formação de uma espécie orto-metalada. Por cloração fotoquímica de A por CH_2Cl_2 forma-se $[\text{Re}_2\text{Cl}_3(\text{dppe})_4]$, enquanto que o composto oxo $[\text{ReOCl(dppe)}_2]$ é gerado na presença de dioxigénio; fotólise de uma solução de A na ausência de qualquer substrato conduz à formação de uma espécie, $[\text{Re}_2\text{Cl}_2(\text{dppe})_3]$, possivelmente dimérica e orto-metalada.