

THE REACTIONS OF DECACARBONYLRHENIUM WITH SOME ORGANO-PHOSPHANES AND PHOSPHITES

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(Received August 20th, 1979)

Summary

The reactions between $\text{Re}_2(\text{CO})_{10}$ and a number of organo-phosphanes and phosphites in refluxing xylene have been studied. With $\text{P}(\text{OPh})_3$, the products are 1,2-diaxial- $\text{Re}_2(\text{CO})_8\text{L}_2$ and 1-axial-2,2'-axial, equatorial- $\text{Re}_2(\text{CO})_7\text{L}_3$, whereas with $(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{P}$, 1,2-diaxial- $\text{Re}_2(\text{CO})_8\text{L}_2$ and the metalated complex $\text{Re}(\text{CO})_3\text{L}(\text{L}-\text{H})$ are formed. In the case of $(p\text{-ClC}_6\text{H}_4\text{O})_3\text{P}$, only 1,2-diaxial- $\text{Re}_2(\text{CO})_8\text{L}_2$ was isolated. $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$ and $(\text{cyclohexyl})_3\text{P}$ both yield 1,2-diaxial- $\text{Re}_2(\text{CO})_8\text{L}_2$ and *mer-trans*- $\text{HRe}(\text{CO})_3\text{L}_2$, however, $(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$ gives only the metalated product, $\text{Re}(\text{CO})_4\text{L}-\text{H}$. Formation of the hydrides and metalated compounds is rationalised in terms of the homolysis of the metal-metal bonded dimers to yield metal-centred free radical intermediates. The behaviour of the dimers and the radical intermediates is discussed in terms of the properties of the phosphorus donor ligands.

In the preceding paper [1] we have reported a detailed study of the reaction between $\text{Re}_2(\text{CO})_{10}$ and PPh_3 , in which we were unable to isolate the metal-centred free radicals $[\text{Re}(\text{CO})_4\text{PPh}_3]^\cdot$ and $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2]^\cdot$, although evidence was presented for their existence as reactive intermediates. Our interest in both stabilising such species sufficiently for isolation and examining their reactivity led us to study reactions between $\text{Re}_2(\text{CO})_{10}$ and a range of organo-phosphanes and phosphites.

To date no mononuclear 17-electron complexes of manganese or rhenium containing phosphorus donor ligands have been isolated as stable crystalline solids, however, there is irrefutable X-ray crystallographic evidence that $\text{Co}(\text{CO})_3\text{L}$ ($\text{L} = \text{bis}(\text{diphenyl-phosphine})\text{maleic anhydride}$) is a stable 19-electron monomer [2]. In this case, it is likely that the electron-withdrawing nature of the anhydride group lowers the unpaired electron density at the metal atom, thereby making the metal more "18-electron-like". In our study [1] of the Re_2 -

(CO)₁₀-PPh₃ reaction, metal centred radicals were observed to undergo rapid hydrogen abstraction reactions, thereby yielding diamagnetic metal hydrides. In seeking to stabilise the mononuclear rhenium-centred radicals, we investigated reactions between Re₂(CO)₁₀ and organo-phosphanes and phosphites that are approaching the extremes of the range of electronically transmitted effects, as well as those capable of shielding the metal atom because of their bulk [3].

A preliminary account of this work has been published [4].

Experimental

All reactions were performed under dry deoxygenated nitrogen. Solvents were purified and dried by standard techniques and were degassed by repeated freeze-pump-thaw cycles immediately prior to use. Preparative TLC separations were performed on silica gel (Merck type PF₂₅₄), 0.3 mm thickness on glass plates (20 cm × 20 cm). Elution was with a mixed solvent consisting of 3 parts 80–100 petroleum ether and 1 part ethyl acetate. The plates were washed with methanol prior to use.

Infrared spectra were recorded on Perkin Elmer 157 and 457 spectrometers as solutions in chloroform unless otherwise stated. UV-visible spectra were recorded on a Pye-Unicam SP8000. PMR spectra were recorded on a Perkin Elmer R 32 spectrometer, operating at 90 MHz and 35°C. ³¹P NMR spectra were recorded on a Bruker HFX-90 operating at 36.4 MHz and chemical shifts are quoted with respect to H₃PO₄. Mass spectra were recorded on an AEI MS9 operating at 70 eV and 100–150°C. Microanalyses were performed by Butterworths Ltd., Teddington, Middlesex. Molecular weight determinations were performed by freezing point depression.

The reaction of Re₂(CO)₁₀ and P(OPh)₃

Re₂(CO)₁₀ (0.66 g, 1.01 mmol) and P(OPh)₃ (2.84 g, 9.1 mmol) were heated together in refluxing xylene (15 ml) for 17.5 h. After this time, the solvent was removed in vacuo and the oily residue extracted with n-hexane. Concentration of the extract gave white crystals (172 mg, 15% based in 1,2-diax-Re₂(CO)₈-[P(OPh)₃]₂; m.p. 157–158°C; ν(C≡O): 2030w, 1984vs cm⁻¹; ³¹P NMR: 117.9 ppm (s); UV (CH₃CN): 316 nm (ε, 14661); anal. found: C, 43.60; H, 2.50; P, 5.41; C₄₄H₃₀O₁₄P₂Re₂ calcd.: C, 43.50; H, 2.49; P, 5.09%; Mol. weight (in C₆H₆), found 1364; calculated, 1216).

The hexane insoluble material was separated by preparative TLC into two major components. The first gave a further crop of 1,2-diax-Re₂(CO)₈-[P(OPh)₃]₂. The second gave a colourless solid (m.p. 130–131°C; ν(C≡O): 2065w, 2000(sh), 1980s, 1962s, 1912m cm⁻¹; anal. found: C, 49.41; H, 3.21; P, 5.95; C₆₁H₄₅O₁₆P₃Re₂ calcd.: C, 48.86; H, 3.00; P, 6.21%).

The reaction of Re₂(CO)₁₀ and tri(o-tolyl)phosphite

A mixture of Re₂(CO)₁₀ (0.33 g, 0.0507 mmol) and tri(o-tolyl)phosphite (1.61 g, 4.6 mmol) was heated in xylene (15 ml) under reflux for 16 h. After this time the solvent was removed, leaving an oily residue. Preparative TLC yielded a white solid which was recrystallised from hexane to give white needles, (245 mg, 37.8% based on 1,2-diax-Re₂(CO)₈[P(OC₆H₄CH₃)₃]₂; m.p.

197–199°C; $\nu(\text{C}\equiv\text{O})$: 2030w, 1983vs cm^{-1} ; UV (CH_3CN): 317 nm (ϵ , 14823); anal. found: C, 46.82; H, 3.26; P, 4.80, $\text{C}_{50}\text{H}_{42}\text{O}_{14}\text{P}_2\text{Re}_2$ calcd.: C, 46.22; H, 3.23; P, 4.77%).

When the above reaction was allowed to proceed for 52.5 h a different major product was isolated by TLC as white crystals (150 mg, 16% based on $\text{Re}(\text{CO})_3\text{-L}(\text{L}-\text{H})$ ($\text{L} = \text{P}(\text{OC}_6\text{H}_4\text{CH}_3)_3$); m.p. 109–111°C; $\nu(\text{C}\equiv\text{O})$: 1982s, 1968s, 1915m cm^{-1} ; anal. found: C, 55.99; H, 4.70; P, 6.69, $\text{C}_{45}\text{H}_{41}\text{O}_9\text{P}_2\text{Re}$ calcd.: C, 55.50; H, 4.21; P, 6.37%, mass spec. (m/e): 972 (M^+), 944 ($M - \text{CO}$), 916 ($M - 2 \text{CO}$) 888 ($M - 3 \text{CO}$); PMR (CDCl_3) (δ , ppm): 7.01 (m, 23H), 2.03 (m, 18H).

The reaction of $\text{Re}_2(\text{CO})_{10}$ with tri(o-tolyl)phosphane

$\text{Re}_2(\text{CO})_{10}$ (0.33 g, 0.507 mmol) and tri(o-tolyl)phosphane (1.45 g, 4.7 mmol) were heated together in xylene (15 ml) for 23.5 h. The solvent was then removed in vacuo and TLC separation gave the major product as white crystals, 125 mg, 41% based on $\text{Re}(\text{CO})_4(\text{L}-\text{H})$ ($\text{L} = \text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3$) (m.p. 174–175°C; $\nu(\text{C}\equiv\text{O})$: 2080s, 1975vs, 1925s cm^{-1} ; anal. found: C, 50.14; H, 3.38; P, 5.48, $\text{C}_{25}\text{H}_{19}\text{O}_4\text{PRe}$ calcd.: C, 50.00, H, 3.33; P, 5.16; mass spec. (m/e): 600 (M^+) 572 ($M - \text{CO}$), 544 ($M - 2 \text{CO}$), 516 ($M - 3 \text{CO}$), 488 ($M - 4 \text{CO}$); PMR (CDCl_3) (δ , ppm): 7.10 (m, 12H), 2.42 (broad d, 2H), 2.10 (s, 6H)).

The reaction of $\text{Re}_2(\text{CO})_{10}$ and tri(p-tolyl)phosphine

$\text{Re}_2(\text{CO})_{10}$ (0.33 g, 0.507 mmol) and tri(p-tolyl)phosphane (1.45 g, 4.7 mmol) were heated together in xylene (15 ml) for 16 h. The solvent was then removed in vacuo and the two major products separated by preparative TLC. Band 1 was identified as $\text{HRe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3]_2$ ($\nu(\text{C}\equiv\text{O})$: 1935s cm^{-1} ; mass spec. (m/e): 878 (M^+), 850 ($M - \text{CO}$), 822 ($M - 2 \text{CO}$), 794 ($M - 3 \text{CO}$)). Band 2 was identified as 1,2-diax- $\text{Re}_2\text{CO}_8[\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3]_2$ ($\nu(\text{C}\equiv\text{O})$: 2000w, 1958s cm^{-1} ; mass spec. (m/e): 1202 (M^+)).

The reaction of $\text{Re}_2(\text{CO})_{10}$ and tri(cyclohexyl)-phosphane

A mixture of $\text{Re}_2(\text{CO})_{10}$ (0.33 g, 0.507 mmol) and tri(cyclohexyl)phosphane (0.987 g, 3.5 mmol) in xylene was heated under reflux for 20 h. The solvent was removed in vacuo and the residue recrystallised several times from xylene-methylated spirit to yield white crystals (80 mg, 14% based on 1,2-diax- $\text{Re}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_{11})_3]_2$; m.p. 248°C(d); $\nu(\text{C}\equiv\text{O})$: 1997w, 1951s cm^{-1} ; UV (CH_3CN): 295 nm (ϵ , 3976); anal. found: C, 44.34; H, 5.52; P, 5.10, $\text{C}_{44}\text{H}_{66}\text{O}_8\text{P}_2\text{Re}_2$ calcd.: C, 45.68; H, 5.71; P, 5.35%).

When the reaction was run for periods of 24 h or greater a second product was formed which was isolated by preparative TLC. This was identified as $\text{HRe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ ($\nu(\text{C}\equiv\text{O})$: 1933s cm^{-1} ; mass spec. (m/e): 830 (M^+), 802 ($M - \text{CO}$), 774 ($M - 2 \text{CO}$), 746 ($M - 3 \text{CO}$)).

The reaction of $\text{Re}_2(\text{CO})_{10}$ and tri(p-chlorophenyl)phosphite

$\text{Re}_2(\text{CO})_{10}$ (0.33 g, 0.507 mmol) and tri(p-chlorophenyl)phosphite (1.86 g, 4.4 mmol) were heated together in xylene (15 ml) for 16 h. Removal of the solvent followed by TLC separation yielded white crystals (110 mg, 16% based on 1,2-diax- $\text{Re}_2(\text{CO})_8[\text{P}(\text{OC}_6\text{H}_4\text{Cl}_3)]_2$; anal. found: C, 37.71; H, 1.94; Cl, 14.41; P, 4.29, $\text{C}_{44}\text{H}_{24}\text{Cl}_6\text{O}_4\text{P}_2\text{Re}_2$ calcd.: C, 37.12; H, 1.68; Cl, 14.94; P, 4.49%).

Results and discussion

In seeking to stabilize radicals such as $[\text{Re}(\text{CO})_4\text{L}^\cdot]$ and $[\text{Re}(\text{CO})_3\text{L}_2^\cdot]$ we employed the strongly electron donating phosphine, $\text{P}(\text{cyclohexyl})_3$ [3], in the hope that an increase in electron density at the metal centre of any 17-electron free radical would make the radical more "18-electron-like", thereby enhancing its stability. Furthermore, the large cone angle of the ligand of 170° (c.f. 145° for PPh_3) might perhaps shield a metal-centred radical such as $\text{Re}(\text{CO})_3\text{L}_2^\cdot$ from solvent attack. Brown et al. [4] have shown the radical $[\text{Mn}(\text{CO})_3(\text{Pn-Bu}_3)_2^\cdot]$ to have considerable stability in solution. This contains a much smaller phosphane (cone angle, 132°) but one having very similar ligating properties to $\text{P}(\text{cyclohexyl})_3$. However, we were unable to isolate any odd-electron species, the principle products being 1,2-diaxial- $\text{Re}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ and *mer-trans*- $\text{HRe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_{11})_3]_2$, analogous to the $\text{PPh}_3\text{-Re}_2(\text{CO})_{10}$ reaction [4]. We again suggest that the radical $\{\text{Re}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_{11})_3]_2^\cdot\}$ is the precursor of the hydride and it is noteworthy that Brown et al [5] isolated an analogous hydride from a solution shown to contain $\{\text{Mn}(\text{CO})_3[\text{Pn-Bu}_3]_2^\cdot\}$.

Brown et al [5] also reported production of $\{\text{Mn}(\text{CO})_3[\text{P}(\text{OEt}_3)_2]^\cdot\}$ by photolysis of $\text{Mn}_2(\text{CO})_7[\text{P}(\text{OEt})_3]_3$ and others [6] have reported $\text{Re}_2(\text{CO})_8\text{-}[\text{P}(\text{OPh})_3]_2$ to be paramagnetic in benzene solution. We have, therefore, investigated the reaction of $\text{Re}_2(\text{CO})_{10}$ with these phosphites as well as those of some related ligands.

The reaction between $\text{Re}_2(\text{CO})_{10}$ and $\text{P}(\text{OEt})_3$ in refluxing xylene is extremely complex yielding a mixture of some seven products which were not investigated in detail. However, when $\text{P}(\text{OPh})_3$ is employed two dimeric products were isolated after 17.5 h. These proved to be $\text{Re}_2(\text{CO})_8[\text{P}(\text{OPh})_3]_2$ and $\text{Re}_2(\text{CO})_7[\text{P}(\text{OPh})_3]_2$, the second of which had not been previously reported. In our previous paper [4], we erroneously identified $\text{Re}_2(\text{CO})_7[\text{P}(\text{OPh})_3]_2$ as $\text{Re}(\text{CO})_3\text{L}(\text{L-H})$ ($\text{L} = \text{P}(\text{OPh})_3$). The infrared spectrum of this compound is not identical in the pattern of bands to that of $\text{Mn}_2(\text{CO})_7[\text{P}(\text{OEt})_3]_3$ or those of both isomers of $\text{Re}_2(\text{CO})_7(\text{PMePh}_2)_3$ [8]. No structural assignment has been made for the manganese complex and the PMePh_2 complexes have been assigned as the 1-equatorial-2,2'-diequatorial and 1-axial-2,2'-diequatorial isomers.

In view of these differences in infrared spectra and the fact that $\text{Re}_2(\text{CO})_7\text{-}[\text{P}(\text{OPh})_3]_3$ is likely to be formed by direct substitution into 1,2-diax- $\text{Re}_2(\text{CO})_8\text{-}[\text{P}(\text{OPh})_3]_2$ we tentatively assigned it as the 1-axial-2,2'-axial, equatorial isomer. We were unable to isolate any other products from this reaction in quantities sufficient for characterisation, although other faint spots appeared on thin layer chromatograms from this reaction and those run for longer periods of time.

We were also unable to confirm the dissociation of $\text{Re}_2(\text{CO})_8[\text{P}(\text{OPh})_3]_2$ in solution by either molecular weight measurements or by the NMR method of establishing paramagnetism [9].

Reaction between $\text{Re}_2(\text{CO})_{10}$ and the more bulky ligand (*o*- $\text{CH}_3\text{C}_6\text{H}_4\text{O}$) $_3\text{P}$ (cone angle 165°) yielded the dimer, 1,2-diax- $\text{Re}_2(\text{CO})_8[(\text{o-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{P}]_2$, however prolonged reaction lead to *fac*- $\text{Re}(\text{CO})_3\text{L}(\text{L-H})$ ($\text{L} = (\text{o-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{P}$). Presumably this arises as a result of homolysis of the dimer $\text{Re}_2(\text{CO})_7[(\text{o-CH}_3\text{-}$

$\text{C}_6\text{H}_4\text{O})_3\text{P}]_3$, the increased bulk of the phosphite ligand rendering this a more facile process than in the case of the $\text{P}(\text{OPh})_3$ analogue. NMR data indicate metalation has taken place at the aromatic ring rather than the methyl group, thereby forming a sterically favoured five-membered ring [10]. Despite an extensive search we have been unable to identify $\text{Re}(\text{CO})_4(\text{L}-\text{H})$, the metalated product which may be formed from the complementary radical arising from homolysis of the dimer, or $\text{HRe}(\text{CO})_4[(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{P}]$, which would be expected if metalation arises via Alper's mechanism [11] for decomposition of the dimer.

Reaction of $(p\text{-ClC}_6\text{H}_4\text{O})_3\text{P}$ with $\text{Re}_2(\text{CO})_{10}$ yields only 1,2-diaxial- $\text{Re}_2(\text{CO})_8[(p\text{-ClC}_6\text{H}_4\text{O})_3\text{P}]_2$, even after a reaction of 100 h duration. In none of these reactions involving phosphites were any hydride complexes observed, in complete contrast to those involving PPh_3 and $\text{P}(\text{cyclohexyl})_3$.

$\text{Re}(\text{CO})_3(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)$ is only a minor product of the reaction of $\text{Re}_2(\text{CO})_{10}$ and PPh_3 and was not observed in the reaction of the bulkier ligand $\text{P}(\text{cyclohexyl})_3$. In order to investigate the effect of ligand bulk in these reactions we examined the reaction between $\text{Re}_2(\text{CO})_{10}$ and $(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$ (cone angle, 194°). The only product isolated from this reaction is the metalated complex $\text{Re}(\text{CO})_3(\text{L}-\text{H})\text{L}$ ($\text{L} = (o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$). The infrared and PMR spectra of this complex are very similar to those reported for the manganese analogue [12]. In particular, the PMR spectrum shows absorptions at δ 7.10, 2.42 and 2.10 ppm of relative intensities 12 : 2 : 6. This clearly indicates that metalation has occurred via a methyl group rather than via the ring. We are, however, uncertain as to whether the broad doublet at 2.42 ppm arises as a consequence of $^{31}\text{P}-^1\text{H}$ coupling of ca. 9 Hz magnitude or from resonances due to inequivalent geminal protons.

The reaction of $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$ with $\text{Re}_2(\text{CO})_{10}$ yields 1,2-diaxial- $\text{Re}_2(\text{CO})_8[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_2$ and *mer-trans*- $\text{HRe}(\text{CO})_3[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}]_2$, just as in the case with PPh_3 . It is therefore clear that the preferred formation of $(\text{OC})_4\text{Re}[\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_2]$ by the *ortho* isomer is sterically controlled. The extreme bulk of the phosphane presumably destabilises the 1,2-diaxial dimer, the radical so formed undergoing metalation rather than hydride formation. Furthermore, it is clear that an alkyl group can compete effectively with an aromatic ring in a metalation reaction when the product contains the favoured five membered ring.

In summary, it is evident that the reactivity of both substituted metal-metal bonded dimers, of the type $\text{M}_2(\text{CO})_n\text{L}_{10-n}$, and the radicals formed via homolysis of the metal-metal bond is dependent on the nature of L. While the behaviour of the dimers can be rationalised in terms of the bulk of the phosphorus donor ligand and the strength of the metal-metal bonds as measured by $\sigma \rightarrow \sigma^*$ transitions observed in the UV spectra [13], the reactivity of the radicals cannot be completely systematised. Thus, in rationalising the propensity for hydride formation or metalation, the behaviour of most radicals is governed by the size of the phosphorus donor ligand and size of metalated ring. However, $\text{P}(\text{cyclohexyl})_3$ (cone angle, 179°) yields a hydride, while $(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{P}$ (cone angle, 165°) and $(o\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$ (cone angle, 194°) give metalated products. Molecular models show $\text{P}(\text{cyclohexyl})_3$ should be capable of undergoing metalation at the γ -carbon atom. Presumably the greater flexibility of this

molecule compared to the tri-*ortho*-tolyl-phosphane and phosphite means that the attainment of the correct transition state geometry is a less likely occurrence.

Acknowledgements

We thank the Royal Borough of Kingston upon Thames for financial support (to D.J.C.) and Dr. S. Robinson of King's College, London, for recording the ^{31}P NMR spectra. We also acknowledge useful discussions with Professor A.J. Poë.

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