Photochemical Reactions of $\text{Re(CO)}_5\text{Br}$ with $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$ (n = 1, 2, 3)

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The complexes fac-[Re(CO)₃Br{Ph₂P(S)(CH₂)_nP(S)Ph₂}] [**la**, n = 1; **2a**, n = 2; **3a**, n = 3] and [Re₂(CO)₈Br₂{ μ -Ph₂P(S)(CH₂)_nP(S)Ph₂}] [**1b**, n = 1; **2b**, n = 2; **3b**, n = 3] have been prepared by the photochemical reaction of Re(CO)₅Br with Ph₂P(S)(CH₂)_nP(S)Ph₂. The products have been characterized by elemental analysis, mass spectroscopy, FT-IR and ³¹ P-[¹H]-NMR spectrometry. The results suggest *cis*-chelate bidentate coordination of the ligand in *fac*-**1a** – **3a** and *cis*-bridging bidentate coordination of the ligand between two metals in **1b** – **3b**.

Key words: Diphosphines, Metal Carbonyls

Introduction

The use of biphosphines, $Ph_2P(CH_2)_nPPh_2$, as chelating or bridging ligand is well known. The chemistry of complexes of dppm, $Ph_2PCH_2PPh_2$, was reviewed by Puddephatt [1], and more recently by Poilblanc [2, 3]. Work on related diphosphine disulfide ligands has been much less extensive, but P,S-coordination has been reported for $Ph_2PCH_2P(S)Ph_2$ [4, 5], and S- or S,S-coordination for $Ph_2P(S)CH_2P(S)Ph_2$ [6–8]. Metal complexes of phosphine and arsine sulphides and selenides have been reviewed [9].

We have recently reported the preparation and characterization of new complexes fac-[Re(CO)₃Br {R₂P(S)P(S)R₂}] and [Re₂(CO)₈Br₂{cis- μ -R₂P(S) P(S)R₂}] (R = Me, Et, Pr^{*n*}, Bu^{*n*}, Ph), which were prepared by photochemical reactions between Re(CO)₅Br with Ph₂P(S) P(S)Ph₂ [10]. We have also previously discovered a photochemical reaction of M(CO)₆ (M = Mo, W) with R₂P(S)P(S)R₂ (R = Me, Et, Pr^{*n*}, Bu^{*n*}) to

give the chelate complexes $[M(CO)_4 \{R_2P(S)P(S)R_2\}]$ (R = Me, Et, Prⁿ, Bu_n) [11–13], where the ligand is presumed to adopt the expected *cis*-chelate bidentate coordination. However, in certain cases, the ligand bridges between two metals affording $[M_2(CO)_{10} \{\mu$ - $R_2P(S)P(S)R_2\}]$ (R = Me, Et, Prⁿ, Buⁿ) [14] as secondary products.

In this paper we report the preparation and characterization of new complexes *fac*-[Re(CO)₃Br{Ph₂P(S) (CH₂)_nP(S)Ph₂}] [**la**, n = 1; **2a**, n = 2; **3a**, n = 3] and [Re₂(CO)₈Br₂ { μ -Ph₂P(S)(CH₂)_nP(S)Ph₂}] [**1b**, n = 1; **2b**, n = 2; **3b**, n = 3] which were prepared by photochemical reactions between Re(CO)₅Br with Ph₂P(S)(CH₂)_nP(S)Ph₂ (n = 1, 2, 3). The results of suggest *cis*-chelate bidentate coordination of the ligand in *fac*-[Re(CO)₃Br{Ph₂P(S)(CH₂)_nP(S)Ph₂}] and bridging coordination of the ligand between two metals in Re₂(CO)₈Br₂{ μ -Ph₂P(S)(CH₂)_nP(S)Ph₂}] (n =1,2,3).

Result and Discussion

The photogeneration of $M(CO)_5$ from $M(CO)_6$ (M = Cr, Mo or W) has been extensively studied. These 16-electron $M(CO)_5$ fragments react avidly with any available donor to form $M(CO)_5L$ species, and where L is a chelating bidentate ligand, rapid continuation to the chelating $M(CO)_4L$ or bridging $M_2(CO)_{10}(\mu-L)$ products may occur [10–14, 16]. The photochemical reactions of Re(CO)₅Br with Ph₂P(S)(CH₂)_nP(S)Ph₂ (n = 1, 2, 3) proceed in this expected manner to yield the hitherto unknown series of complexes **1a**-**3a** and **1b**-**3b**.

The infrared spectra of the [Re(CO)₃BrL-L] compounds are consistent with a fac-structure in which ligands L-L are *cis* to the Br. There are three strong carbonyl bands allowing an unequivocal assignment of [Re(CO)₃BrL-L] compounds as the fac-isomer of $C_{\rm S}$ symmetry. The three carbonyl stretching vibrations belong to the symmetry classes of the point group as follows ($\tau = 2A'' + A'$) [17, 18]. The infrared spectra of the [Re₂(CO)₈Br₂{ $cis-\mu$ -L-L}] compounds are consistent with a structure in which the donor centers of L-L are *cis* to the Br. As expected, four bands arising from v(CO) vibrations are seen for each complex 1b – **3b** which presumably have *local* C_{2v} symmetry of the $M(CO)_4$ unit. The v(CO) modes of 1a - 3a and 1b - 3bare shifted to lower wavenumbers when compared with the starting Re(CO)₅Br molecules [19].

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Fig. 1. The photochemical reactions of $\text{Re}(\text{CO})_5\text{Br}$ with $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$ (n = 1, 2, 3).

The ³¹P-[¹H] NMR spectra of complexes **1a**-**3a** and **1b**-**3b**, show only one signal in each case. The $\delta_{\rm P}$ values of the coordinated ligands are at higher field than those of the free ligands, and the coordinated *cis*-bridging ligands are at higher field compared to ligands coordinated in a *cis*-chelating mode [20].

The mass spectral data of 1a-3a and 1b-3b are given in Table 3. The mass spectra show fragmentation *via* successive loss of CO groups and fragmentation of the organic ligands.

We therefore have shown that the photochemical reactions between $\text{Re}(\text{CO})_5\text{Br}$ and $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_n$ $\text{P}(\text{S})\text{Ph}_2$ (n = 1, 2, 3) leads to two series of products, which have the donor center in metal *cis*-position and *cis* to the halide ligand.

Experimental Section

General

Reactions were carried out under dry nitrogen by using Schlenk techniques. All solvents were dried and degassed prior to use. Elemental analyses were carried out using a LECO-CHNS-O-9320 instrument by the Technical and Scientific Research Council of Turkey, TUBITAK. FT-IR spectra were recorded on samples in hexane at the Ege University on a Mattson 1000 FT spectrophotometer. ³¹P[¹H] NMR spectra were recorded in CDC1₃/CD₂C1₂ at UCL on a BRUKER DPX-400 and 400 MHz High Performance Digital Ft-NMR instrument (TUBITAK). Electron impact mass spectra were recorded on Micromass VG Platform-II LC-MS at TÜBITAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor. Pentane, benzene, hexane, CH₂Cl₂, Me₂CO, toluene and silica gel were purchased from Merck, and Re(CO)₅Br, was purchased from Aldrich. dppm(S)₂, dppe(S)₂ and dppp(S)₂ were prepared by literature methods [15].

The complexes, fac-[Re(CO)₃Br{Ph₂P(CH₂)_nPPh₂}] **1a**-**3a** and [Re₂(CO)₈Br₂{ μ -R₂P(S)P(S)R₂}], were prepared by the photochemical reactions of Re(CO)₅Br with Ph₂P(CH₂)_nPPh₂ (n = 1, dppm; 2, dppe; 3, dppp) and obtained in 40–60% yield by similar methods of which the following is typical.

Syntheses

The components $\text{Re}(\text{CO})_5\text{Br}$ (0.8 g, 2 mmol) and dppm(S)₂ (0.45 g, 1 mmol) were dissolved in tetrahydrofuran (80–100 ml) and the solution was irradiated for 2 h using a 400 W medium pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the colour of the solution changed from colourless to dark yellow. After the irradiation the solvent was evaporated in a vacuum resulting in a dark-yellow solid which was extracted into dichloromethane (10 ml). Addition of petroleum ether (50 ml) resulted in precipitation of a dark yellow solid which was washed with petroleum ether dried in a vacuum, and shown to be *fac*-[Re(CO)₃Br{Ph₂P(S)CH₂P(S)Ph₂}], **1a**, (42% yield). The yellow solution was evaporated and the residue separated chromatographically through a column packed with silica gel using *n*-pentane as an eluant. A yellow fraction was isolated and dried *in vacuo* to give $[Re_2(CO)_8Br_2{\mu-Ph_2 P(S)CH_2P(S)Ph_2}]$, **1b**, (39% yield).

Re(CO)₅(dppmS₂)Br,**1a**: Yield: 40%. IR (KBr): v = 2018 (m, C=O), 1916 (m, C=O), 1876 (m, C=O). $-{}^{31}P[{}^{1}H]$ NMR (400 MHz, DMSO): $\delta = 36.24$. -MS (EI, 70 eV): m/z (%) = 798 (35) [M⁺]; 770 (25) [M⁺–CO]; 742 (10) [M⁺–2CO]; 714 (20) [M⁺–3CO]. $-C_{28}H_{22}O_3ReP_2S_2Br$ (798.7): calcd. C 42.11, H 2.78, S 8.03; found C 42.38, H 2.51, S 8.34.

Re(CO)₅(dppeS₂)Br, **2a**: Yield: 50%. IR (KBr): v = 2008 (m, C=O), 1914 (m, C=O), 1874 (m, C=O). $-^{31}P[^{1}H]$ NMR (400 MHz, DMSO): $\delta = 32.71. -$ MS (EI, 70 eV): m/z (%) = 812 (15) [M⁺]; 784 (35) [M⁺ - CO]; 756 (90) [M⁺ - 2CO]; 728 (75) [M⁺ - 3CO]; 648 (20) [M⁺ - 3CO - Br]. - C₂₉H₂₄O₃ReP₂S₂Br (812.7): calcd. C 42.86, H 2.98, S 7.89; found: C 42.62, H 2.81, S 7.95.

Re(CO)₅(dpppS₂)Br, **3a**: Yield: 40%. IR (KBr): v = 2006 (m, C=O), 1982 (m, C=O), 1925 (m, C=O). $-{}^{31}P[{}^{1}H]$ NMR (400 MHz, DMSO): $\delta = 40.25 - MS$ (EI, 70 eV): m/z (%) = 826 (10) [M⁺]; 798 (100) [M⁺-CO]; 770 (50) [M⁺-2CO]; 662 (20) [M⁺-3CO-Br]. $-C_{30}H_{26}O_{3}ReP_{2}S_{2}Br$ (826.7): calcd. C 43.59, H 3.17, S 7.76; found C 43.33, H 3.29, S 7.55.

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 $\begin{array}{l} Re_2(CO)_8(\mu\text{-dppeS}_2)Br_2 \ \textbf{2b}: \ Yield: \ 40\%. \ IR \ (KBr): \ \nu = \\ 2105 \ (m, \ C=O), \ 2018 \ (m, \ C=O), \ 1916 \ (m, \ C=O), \ 1876 \ (m, \\ C=O). \ - \ ^{31}P[^1H] \ NMR \ (400 \ MHz, \ DMSO): \ \delta = \ 45.86. \ - \\ MS \ (EI, \ 70 \ eV): \ m/z \ (\%) \ = \ 812 \ (25) \ [M^+ - ReBr(CO)_4-\\ CO]; \ 784 \ (20) \ [M^+ - ReBr(CO)_4-2CO]; \ 756 \ (90) \ [M^+ - \\ ReBr(CO)_4-3CO]; \ 728 \ (90) \ [M^+ - \ ReBr(CO)_4-4CO]; \ 648 \\ (20) \ [M^+ - ReBr(CO)_4-4CO-Br]. \ - \ C_{34}H_{24}O_8Re_2P_2S_2Br_2 \\ (1218.4): \ calcd. \ C \ 33.50, \ H \ 1.98, \ S \ 5.26; \ found \ C \ 33.41, \\ H \ 1.93, \ S \ 5.34. \end{array}$

$$\begin{split} & \text{Re}_2(\text{CO})_8(\mu\text{-dppp}S_2)\text{Br}_2, \textbf{3b}: \text{Yield: } 40\%. \text{ IR (KBr): } \nu = \\ & 2106 \text{ (m, C=O), } 2010 \text{ (m, C=O), } 1983 \text{ (m, C=O), } 1924 \text{ (m, } \\ & \text{C=O).} - {}^{31}\text{P}[{}^{1}\text{H}] \text{ NMR (} 400 \text{ MHz, } \text{DMSO}): \delta = 53.11. - \\ & \text{MS (EI, } 70 \text{ eV}): m/z \text{ (\%)} = 854 \text{ (30) } [\text{M}^+ - \text{Re}\text{Br}(\text{CO})_4]; \\ & 826 \text{ (5) } [\text{M}^+ - \text{Re}\text{Br}(\text{CO})_4\text{-CO}]; 798 \text{ (20) } [\text{M}^+ - \text{Re}\text{Br}(\text{CO})_4\text{-} \\ & 2\text{CO}]; 770 \text{ (10) } [[\text{M}^+ - \text{Re}\text{Br}(\text{CO})_4\text{-} 3\text{CO}]; 742 \text{ (10) } [\text{M}^+ - \\ & \text{Re}\text{Br}(\text{CO})_4\text{-} 4\text{CO}]; 762 \text{ (30) } [\text{M}^+ - \text{Re}\text{Br}(\text{CO})_4\text{-} 4\text{CO}\text{-Br}]. - \\ & \text{C}_{35}\text{H}_{26}\text{O}_8\text{Re}_2\text{P}_2\text{S}_2\text{Br}_2 \text{ (1232.8): calcd. C 34.10, H 2.13, } \\ & \text{S 5.20; found C 34.19, H 2.21, S 5.29.} \end{split}$$

For the mass spectral data relative intensities are given in parentheses; probable assignments in square brackets. For all assignments the most abundant isotopes of Re and Br have been selected (187 Re, 62.9% abundant, 79 Br, 50.5% abundant).

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