# Photochemical Reactions of $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}$ with $\mathrm{Ph}_{2} \mathbf{P}(\mathbf{S})\left(\mathrm{CH}_{2}\right)_{n} \mathbf{P}(\mathbf{S}) \mathrm{Ph}_{2}(\boldsymbol{n}=\mathbf{1 , 2 , 3})$ 

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The complexes fac- $\left[\mathrm{Re}(\mathrm{CO})_{3} \mathrm{Br}\left\{\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}\right\}\right]$ [la, $n=1 ; \mathbf{2 a}, n=2 ; \mathbf{3 a}, n=3]$ and $\left[\mathrm{Re}_{2}(\mathrm{CO})_{8} \mathrm{Br}_{2}\{\mu-\right.$ $\left.\left.\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}\right\}\right][\mathbf{1 b}, n=1 ; \mathbf{2 b}, n=2 ; \mathbf{3 b}, n=$ 3] have been prepared by the photochemical reaction of $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}$ with $\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}$. The products have been characterized by elemental analysis, mass spectroscopy, FT-IR and ${ }^{31} \mathrm{P}-\left[{ }^{1} \mathrm{H}\right]-\mathrm{NMR}$ spectrometry. The results suggest cis-chelate bidentate coordination of the ligand in fac-1a3a and cis-bridging bidentate coordination of the ligand between two metals in $\mathbf{1 b} \mathbf{- 3 b}$.

Key words: Diphosphines, Metal Carbonyls

## Introduction

The use of biphosphines, $\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{n} \mathrm{PPh}_{2}$, as chelating or bridging ligand is well known. The chemistry of complexes of dppm, $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{PPh}_{2}$, 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 $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}$ [4, 5], and S - or $\mathrm{S}, \mathrm{S}$-coordination for $\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S}) \mathrm{CH}_{2} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}[6-8]$. 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- $\left[\operatorname{Re}(\mathrm{CO})_{3} \mathrm{Br}\right.$ $\left.\left\{\mathrm{R}_{2} \mathrm{P}(\mathrm{S}) \mathrm{P}(\mathrm{S}) \mathrm{R}_{2}\right\}\right]$ and $\left[\mathrm{Re}_{2}(\mathrm{CO})_{8} \mathrm{Br}_{2}\left\{c i s-\mu-\mathrm{R}_{2} \mathrm{P}(\mathrm{S})\right.\right.$ $\left.\left.\mathrm{P}(\mathrm{S}) \mathrm{R}_{2}\right\}\right]\left(\mathrm{R}=\mathrm{Me}, \mathrm{Et}, \mathrm{Pr}^{n}, \mathrm{Bu}^{n}, \mathrm{Ph}\right)$, which were prepared by photochemical reactions between $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}$ with $\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S}) \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}$ [10]. We have also previously discovered a photochemical reaction of $\mathrm{M}(\mathrm{CO})_{6}(\mathrm{M}=$ Mo, W) with $\mathrm{R}_{2} \mathrm{P}(\mathrm{S}) \mathrm{P}(\mathrm{S}) \mathrm{R}_{2}\left(\mathrm{R}=\mathrm{Me}, \mathrm{Et}, \mathrm{Pr}^{n}, \mathrm{Bu}^{n}\right)$ to
give the chelate complexes $\left[\mathrm{M}(\mathrm{CO})_{4}\left\{\mathrm{R}_{2} \mathrm{P}(\mathrm{S}) \mathrm{P}(\mathrm{S}) \mathrm{R}_{2}\right\}\right]$ $\left(\mathrm{R}=\mathrm{Me}, \mathrm{Et}, \mathrm{Pr}^{n}, \mathrm{Bu}_{n}\right)$ [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 $\left[\mathrm{M}_{2}(\mathrm{CO})_{10}\{\mu\right.$ $\left.\mathrm{R}_{2} \mathrm{P}(\mathrm{S}) \mathrm{P}(\mathrm{S}) \mathrm{R}_{2}\right\}$ ] ( $\left.\mathrm{R}=\mathrm{Me}, \mathrm{Et}, \mathrm{Pr}^{n}, \mathrm{Bu}^{n}\right)$ [14] as secondary products.
In this paper we report the preparation and characterization of new complexes $f a c-\left[\operatorname{Re}(\mathrm{CO})_{3} \mathrm{Br}\left\{\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\right.\right.$ $\left.\left.\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}\right\}\right][\mathbf{l a}, n=1$; 2a, $n=2$; 3a, $n=3]$ and $\left[\mathrm{Re}_{2}(\mathrm{CO})_{8} \mathrm{Br}_{2}\left\{\mu-\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}\right\}\right][\mathbf{1 b}$, $n=1 ; \mathbf{2 b}, n=2 ; \mathbf{3 b}, n=3$ ] which were prepared by photochemical reactions between $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}$ with $\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2} \quad(n=1,2,3)$. The results of suggest cis-chelate bidentate coordination of the ligand in $f a c-\left[\operatorname{Re}(\mathrm{CO})_{3} \mathrm{Br}\left\{\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}\right\}\right]$ and bridging coordination of the ligand between two metals in $\left.\mathrm{Re}_{2}(\mathrm{CO})_{8} \mathrm{Br}_{2}\left\{\mu-\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}\right\}\right]$ ( $n=$ $1,2,3$ ).

## Result and Discussion

The photogeneration of $\mathrm{M}(\mathrm{CO})_{5}$ from $\mathrm{M}(\mathrm{CO})_{6}(\mathrm{M}=$ Cr , Mo or W) has been extensively studied. These 16-electron $\mathrm{M}(\mathrm{CO})_{5}$ fragments react avidly with any available donor to form $\mathrm{M}(\mathrm{CO})_{5} \mathrm{~L}$ species, and where L is a chelating bidentate ligand, rapid continuation to the chelating $\mathrm{M}(\mathrm{CO})_{4} \mathrm{~L}$ or bridging $\mathrm{M}_{2}(\mathrm{CO})_{10}(\mu-\mathrm{L})$ products may occur $[10-14,16]$. The photochemical reactions of $\mathrm{Re}(\mathrm{CO})_{5} \mathrm{Br}$ with $\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}$ ( $n=1,2,3$ ) proceed in this expected manner to yield the hitherto unknown series of complexes 1a-3a and 1b-3b.

The infrared spectra of the $\left[\operatorname{Re}(\mathrm{CO})_{3} \mathrm{BrL-L}\right]$ compounds are consistent with a $f a c$-structure in which ligands L-L are cis to the Br . There are three strong carbonyl bands allowing an unequivocal assignment of $\left[\operatorname{Re}(\mathrm{CO})_{3} \mathrm{BrL}-\mathrm{L}\right]$ compounds as the $f a c$-isomer of $C_{S}$ symmetry. The three carbonyl stretching vibrations belong to the symmetry classes of the point group as follows ( $\tau=2 \mathrm{~A}^{\prime \prime}+\mathrm{A}^{\prime}$ ) $[17,18]$. The infrared spectra of the $\left[\operatorname{Re}_{2}(\mathrm{CO})_{8} \mathrm{Br}_{2}\{c i s-\mu-\mathrm{L}-\mathrm{L}\}\right]$ compounds are consistent with a structure in which the donor centers of $\mathrm{L}-\mathrm{L}$ are cis to the Br . As expected, four bands arising from $v(\mathrm{CO})$ vibrations are seen for each complex $\mathbf{1 b}$ 3 b which presumably have local $\mathrm{C}_{2 \mathrm{v}}$ symmetry of the $\mathrm{M}(\mathrm{CO})_{4}$ unit. The $v(\mathrm{CO})$ modes of $\mathbf{1 a - 3 a}$ and $\mathbf{1 b} \mathbf{- 3 b}$ are shifted to lower wavenumbers when compared with the starting $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}$ molecules [19].


Fig. 1. The photochemical reactions of $\mathrm{Re}(\mathrm{CO})_{5} \mathrm{Br}$ with $\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}(n=1,2,3)$.

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

The mass spectral data of $\mathbf{1 a - 3 a}$ and $\mathbf{1 b} \mathbf{- 3 b}$ 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 $\mathrm{Re}(\mathrm{CO})_{5} \mathrm{Br}$ and $\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S})\left(\mathrm{CH}_{2}\right)_{n}$ $\mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}(n=1,2,3)$ 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. ${ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR spectra were recorded in $\mathrm{CDC1}_{3} / \mathrm{CD}_{2} \mathrm{C1}_{2}$ 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 LCMS at TÜBITAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartzwalled immersion well reactor. Pentane, benzene, hexane, $\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{Me}_{2} \mathrm{CO}$, toluene and silica gel were purchased from Merck, and $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}$, was purchased from Aldrich. $\operatorname{dppm}(S)_{2}, \operatorname{dppe}(S)_{2}$ and $\operatorname{dppp}(S)_{2}$ were prepared by literature methods [15].

The complexes, fac-[ $\left.\mathrm{Re}(\mathrm{CO})_{3} \mathrm{Br}\left\{\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{n} \mathrm{PPh}_{2}\right\}\right]$ $\mathbf{1 a - 3 a}$ and $\left[\mathrm{Re}_{2}(\mathrm{CO})_{8} \mathrm{Br}_{2}\left\{\mu-\mathrm{R}_{2} \mathrm{P}(\mathrm{S}) \mathrm{P}(\mathrm{S}) \mathrm{R}_{2}\right\}\right]$, were prepared by the photochemical reactions of $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}$ with $\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{n} \mathrm{PPh}_{2}(n=1$, dppm; 2, dppe; 3, dppp) and obtained in $40-60 \%$ yield by similar methods of which the following is typical.

## Syntheses

The components $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}(0.8 \mathrm{~g}, 2 \mathrm{mmol})$ and $\operatorname{dppm}(S)_{2}(0.45 \mathrm{~g}, 1 \mathrm{mmol})$ were dissolved in tetrahydrofuran $(80-100 \mathrm{ml})$ 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 $f a c-\left[\operatorname{Re}(\mathrm{CO})_{3} \mathrm{Br}\left\{\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S}) \mathrm{CH}_{2} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}\right\}\right]$, 1a, ( $42 \%$ yield). The yellow solution was evaporated and the residue separated chromatographically through a col-
umn packed with silica gel using $n$-pentane as an eluant. A yellow fraction was isolated and dried in vacuo to give $\left[\operatorname{Re}_{2}(\mathrm{CO})_{8} \mathrm{Br}_{2}\left\{\mu-\mathrm{Ph}_{2} \mathrm{P}(\mathrm{S}) \mathrm{CH}_{2} \mathrm{P}(\mathrm{S}) \mathrm{Ph}_{2}\right\}\right], \mathbf{1 b},(39 \%$ yield).
$\operatorname{Re}(\mathrm{CO})_{5}\left(\mathrm{dppmS}_{2}\right) \mathrm{Br}, \mathbf{1 a}$ : Yield: $40 \%$. IR ( KBr ): $v=2018$ (m, C=O), 1916 (m, C=O), 1876 ( $\mathrm{m}, \mathrm{C}=\mathrm{O}$ ). - ${ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR (400 MHz, DMSO): $\delta=36.24 .-$ MS (EI, 70 eV ): $\mathrm{m} / \mathrm{z}(\%)=$ 798 (35) $\left[\mathrm{M}^{+}\right] ; 770(25)\left[\mathrm{M}^{+}-\mathrm{CO}\right] ; 742$ (10) [ $\left.\mathrm{M}^{+}-2 \mathrm{CO}\right] ;$ 714 (20) $\left[\mathrm{M}^{+}-3 \mathrm{CO}\right] .-\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{ReP}_{2} \mathrm{~S}_{2} \mathrm{Br}$ (798.7): calcd. C 42.11, H 2.78, S 8.03; found C 42.38, H 2.51, S 8.34.
$\operatorname{Re}(\mathrm{CO})_{5}\left(\mathrm{dppeS}_{2}\right) \mathrm{Br}, \mathbf{2 a}$ : Yield: $50 \%$. IR (KBr): $v=2008$ (m, C=O), 1914 (m, C=O), $1874(\mathrm{~m}, \mathrm{C}=\mathrm{O}) .-{ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR (400 MHz, DMSO): $\delta=32.71$. - MS (EI, 70 eV ): $\mathrm{m} / \mathrm{z}(\%)=$ 812 (15) $\left[\mathrm{M}^{+}\right] ; 784$ (35) $\left[\mathrm{M}^{+}-\mathrm{CO}\right] ; 756$ (90) [ $\left.\mathrm{M}^{+}-2 \mathrm{CO}\right] ;$ 728 (75) [ $\mathrm{M}^{+}-3 \mathrm{CO}$; 648 (20) [ $\left.\mathrm{M}^{+}-3 \mathrm{CO}-\mathrm{Br}\right]$. $\mathrm{C}_{29} \mathrm{H}_{24} \mathrm{O}_{3} \mathrm{ReP}_{2} \mathrm{~S}_{2} \mathrm{Br}$ (812.7): calcd. C 42.86, H 2.98, S 7.89; found: C 42.62, H 2.81, S 7.95 .
$\operatorname{Re}(\mathrm{CO})_{5}\left(\mathrm{dpppS}_{2}\right) \mathrm{Br}$, 3a: Yield: $40 \%$. IR (KBr): $v=2006$ ( $\mathrm{m}, \mathrm{C}=\mathrm{O}$ ), 1982 ( $\mathrm{m}, \mathrm{C}=\mathrm{O}$ ), $1925(\mathrm{~m}, \mathrm{C}=\mathrm{O}) .-{ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR ( 400 MHz, DMSO): $\delta=40.25-\mathrm{MS}$ (EI, 70 eV ): $\mathrm{m} / \mathrm{z}(\%)=826$ (10) $\left[\mathrm{M}^{+}\right] ; 798$ (100) [ $\mathrm{M}^{+}$-CO]; 770 (50) [ $\mathrm{M}^{+}-2 \mathrm{CO}$ ]; 662 (20) [ $\left.\mathrm{M}^{+}-3 \mathrm{CO}-\mathrm{Br}\right] .-\mathrm{C}_{30} \mathrm{H}_{26} \mathrm{O}_{3} \mathrm{ReP}_{2} \mathrm{~S}_{2} \mathrm{Br}$ (826.7): calcd. C 43.59, H 3.17, S 7.76; found C 43.33, H 3.29, S 7.55 .
$\mathrm{Re}_{2}(\mathrm{CO})_{8}\left(\mu-\mathrm{dppmS}_{2}\right) \mathrm{Br}_{2}$, 1b: Yield: $40 \%$. IR (KBr): $v=2105$ ( $\mathrm{m}, \mathrm{C}=\mathrm{O}$ ), 2018 (m, C=O), 1916 (m, C=O), 1876 (m, C=O). $-{ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR ( 400 MHz, DMSO): $\delta=$ 65.25. - MS (EI, 70 eV ): $\mathrm{m} / \mathrm{z}(\%)=799$ (20) $\left[\mathrm{M}^{+}{ }_{-}\right.$ $\left.\operatorname{ReBr}(\mathrm{CO})_{4}-\mathrm{CO}\right] ; 770$ (40) $\left.\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4}-2 \mathrm{CO}\right)\right] ; 742$ (100) $\left[\mathrm{M}^{+}-\mathrm{ReBr}(\mathrm{CO})_{4}-3 \mathrm{CO}\right] ; 714$ (60) $\left[\mathrm{M}^{+}-\mathrm{ReBr}(\mathrm{CO})_{4}{ }^{-}\right.$ 4 CO ]. $-\mathrm{C}_{33} \mathrm{H}_{22} \mathrm{O}_{8} \mathrm{Re}_{2} \mathrm{P}_{2} \mathrm{~S}_{2} \mathrm{Br}_{2}$ (1204.8): calcd. C 32.90, H 1.84, S 5.32; found C 32.87, H 1.89, S 5.39.
$\mathrm{Re}_{2}(\mathrm{CO})_{8}\left(\mu-\mathrm{dppeS}_{2}\right) \mathrm{Br}_{2}$ 2b: Yield: $40 \%$. IR ( KBr ): $v=$ 2105 (m, C=O), 2018 (m, C=O), 1916 (m, C=O), 1876 (m, $\mathrm{C}=\mathrm{O}$ ). $-{ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR ( 400 MHz , DMSO): $\delta=45.86$. MS (EI, 70 eV ): $m / z(\%)=812(25)\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4^{-}}\right.$ CO]; 784 (20) [M $\left.{ }^{+}-\operatorname{ReBr}(\mathrm{CO})_{4}-2 \mathrm{CO}\right] ; 756$ (90) [M ${ }^{+}{ }_{-}$ $\left.\operatorname{ReBr}(\mathrm{CO})_{4}-3 \mathrm{CO}\right] ; 728$ (90) $\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4}-4 \mathrm{CO}\right] ; 648$ (20) $\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4}-4 \mathrm{CO}-\mathrm{Br}\right] .-\mathrm{C}_{34} \mathrm{H}_{24} \mathrm{O}_{8} \mathrm{Re}_{2} \mathrm{P}_{2} \mathrm{~S}_{2} \mathrm{Br}_{2}$ (1218.4): calcd. C 33.50, H 1.98, S 5.26; found C 33.41, H 1.93, S 5.34.
$\operatorname{Re}_{2}(\mathrm{CO})_{8}\left(\mu-\mathrm{dpppS}_{2}\right) \mathrm{Br}_{2}$, 3b: Yield: $40 \%$. IR (KBr): $v=$ 2106 (m, C=O), 2010 (m, C=O), 1983 (m, C=O), 1924 (m, $\mathrm{C}=\mathrm{O}$ ). $-{ }^{31} \mathrm{P}\left[{ }^{1} \mathrm{H}\right]$ NMR ( $400 \mathrm{MHz}, \mathrm{DMSO}$ ): $\delta=53.11$. MS (EI, 70 eV ): $m / z(\%)=854$ (30) $\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4}\right]$; 826 (5) $\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4}-\mathrm{CO}\right] ; 798(20)\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4^{-}}\right.$ 2CO]; 770 (10) $\left[\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4}-3 \mathrm{CO}\right] ; 742\right.$ (10) $\left[\mathrm{M}^{+}{ }_{-}\right.$ $\left.\left.\operatorname{ReBr}(\mathrm{CO})_{4}-4 \mathrm{CO}\right] ; 762(30)\left[\mathrm{M}^{+}-\operatorname{ReBr}(\mathrm{CO})_{4}-4 \mathrm{CO}-\mathrm{Br}\right)\right]$. $\mathrm{C}_{35} \mathrm{H}_{26} \mathrm{O}_{8} \mathrm{Re}_{2} \mathrm{P}_{2} \mathrm{~S}_{2} \mathrm{Br}_{2}$ (1232.8): calcd. C 34.10, H 2.13, S 5.20; found C 34.19, H 2.21, S 5.29.

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 $\left({ }^{187} \mathrm{Re}, 62.9 \%\right.$ abundant, ${ }^{79} \mathrm{Br}, 50.5 \%$ abundant).

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