



PHOTOCHEMICAL REACTIONS OF $[M(CO)_6]$ ($M = Cr, Mo \& W$) WITH QUADRIDENTATE SCHIFF BASES

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ABSTRACT

The new complexes $[(\mu-CO)_2Cr_2(\eta^4-H_2L)_2]$, **1**; $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L)_2]$, [$M = Mo$; **2**, **W**; **3**]; $[(\mu-CO)_2Cr_2(\eta^4-H_2L')_2]$, **4** and $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L')_2]$, [$M = Mo$; **5**, **W**; **6**] have been synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ ($M = Cr, Mo, W$) with three oxygen and one nitrogen donor Schiff base ligands, 2-hydroxybenzamido-2-hydroxybenzaladimine (H_2L) and 2-hydroxybenzamido-2-hydroxy-3-methoxybenzaladimine (H_2L'). The complexes have been characterized by elemental analyses, magnetic studies, infrared spectroscopy. The spectroscopic studies show that H_2L and H_2L' ligands are coordinated to the central metal as tetra-dentate ligands coordinating via their imine N and O donor atoms in (**1-6**).

Key words: Schiff Bases, Metal carbonyl, 2-Hydroxybenzamido-2-hydroxybenzaladimine, 2-Hydroxybenzamido-2-hydroxy-3-methoxybenzaladimine.

INTRODUCTION

Metal complexes of Schiff bases are extensively show bactericidal, biocidal, germicidal, fungicidal and carcinogenic activities. Schiff bases represent an important class of chelating ligands and their metal complexes have been studied widely¹⁻⁴. Recently, interest in the chemistry of transition metal complexes containing Schiff bases has increased greatly⁵. The interest in the synthesis and characterization of transition metal complexes containing a Schiff base lies in their biological and catalytic activity in many reactions. The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural liability and are sensitive to molecular environment. The environment around the metal centre “as coordination geometry, number of coordinated

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ligands and their donor group" is a key factor for metalloprotein to carry out specific physiological function^{6,7}. Numerous Schiff base compounds are often used as ligands in coordination chemistry for their metal binding ability. Unique characteristic properties of Schiff base metal complexes are their ability to reversibly binding oxygen in exoxidation reactions, complexing ability towards some toxic metals, catalytic activity in hydrogenation of olefines and photochromic characteristics⁸⁻¹¹. The Schiff base complexes have continued to attract attention in the part because of the different possible coordination geometries that the ligand may adopt.^{12,13} Their low energy metal to ligand charge transfer [MLCT] transitions make these molecules attractive for luminescence and electron transfer reactions¹⁴.

In the light of the above, the six new complexes (**1-6**) have been prepared for the first time by the photochemical reactions of photogenerated intermediate $M(CO)_5$ THF ($M = Cr, Mo, W$) with two Schiff base ligands, 2-hydroxybenzamido-2-hydroxybenzaladimine (H_2L) and 2-hydroxybenzamido-2-hydroxy-3-methoxybenzaladimine (H_2L') (Fig. 1). Their spectral and magnetic properties of all the complexes were studied in detail.

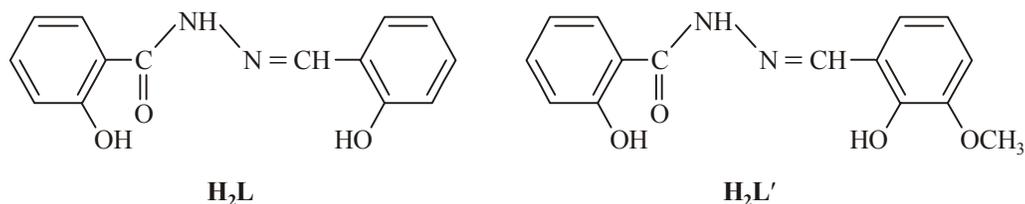


Fig. 1: 2-Hydroxy benzamido-2-hydroxybenzaladimine (H_2L) and 2-Hydroxy benzamido-2-hydroxy-3-methoxybenzaladimine (H_2L')

EXPERIMENTAL

Reactions were carried out under dry argon or in vacuo. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-577) in KBr discs. All the melting points were determined in an open capillary and are uncorrected. All glasswares were oven dried at 120°C. Molecular weights of the complexes were determined cryoscopically in benzene. Organic solvent and silica gel were purchased from E. Merck, and $M(CO)_6$ ($M = Cr, Mo, W$), were purchased from Aldrich.

The Schiff bases H_2L and H_2L' were prepared by the literature method¹⁵. Magnetic susceptibility measurements of the complexes were carried out by Gouy method. UV irradiation was performed with a medium pressure 125W mercury lamp through a quartz bulb.

General procedure for the synthesis of complexes (1-6)

Complexes $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L})_2]$, **1**; $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L})_2]$, [M = Mo; **2**, W; **3**]; $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L}')_2]$, **4** and $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L}')_2]$, [M = Mo; **5**, W; **6**] were prepared by the photochemical reactions of $\text{M}(\text{CO})_5\text{THF}$ (M = Cr, Mo, W) with 2-hydroxy benzamido-2-hydroxybenzaladimine (H_2L) or 2-hydroxy benzamido-2-hydroxy-3-methoxybenzaladimine ($\text{H}_2\text{L}'$). These were obtained in 75-80% yield by similar methods, of which the following is typical; A solution of $\text{Cr}(\text{CO})_6$ (0.22 g; 1 mmole) in 70 mL of THF was irradiated to obtain $\text{Cr}(\text{CO})_5\text{THF}$ with UV light in a quartz vessel under a stream of argon for 2½ hr. at room temperature. A solution of H_2L (0.085 g; 0.33 mmole) in 25 mL of THF was added to the resulting solution of $\text{Cr}(\text{CO})_5\text{THF}$ intermediate. The reaction mixture was irradiated again at room temperature for 2½ hr. at similar conditions. During this irradiation, the solution changed from yellow to brown. The solvent was removed under vacuum to afford a brown airstable solid, which was shown to be $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L})_2]$, **1** (75% yield). Unreacted $\text{Cr}(\text{CO})_6$ was removed by washing the residue several times with light petroleum (40-60°C). The product was recrystallised in benzene.

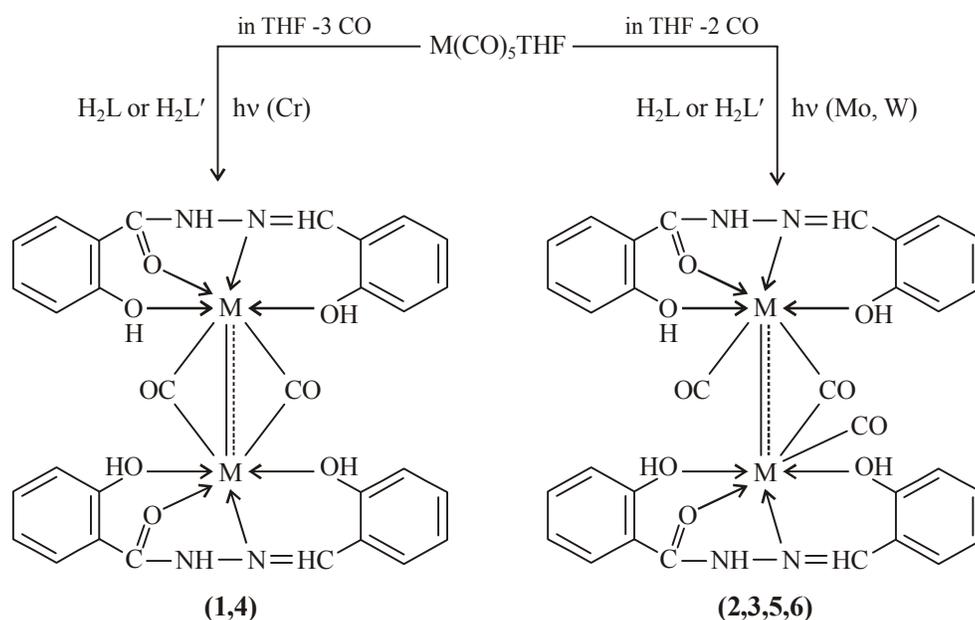


Fig. 2: Representation of photogeneration of $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L})_2]$, **1; $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L})_2]$, [M = Mo; **2**, W; **3**]; $[(\mu\text{-CO})_2\text{Cr}_2(\eta^4\text{-H}_2\text{L}')_2]$, **4** and $[(\mu\text{-CO})\text{M}_2(\text{CO})_2(\eta^4\text{-H}_2\text{L}')_2]$, [M = Mo; **5**, W; **6**]**

Table 1: Physical and analytical data of Complexes (1-6)

Complexes	Empirical formula	Yield (%)	Found (Calculated) (%)			
			C	H	N	Mol. wt.
1	Cr ₂ C ₃₀ H ₂₄ N ₄ O ₈	78	50.53 (53.58)	3.52 (3.56)	8.29 (8.32)	667 (672)
2	Mo ₂ C ₃₁ H ₂₄ N ₄ O ₉	75	45.95 (47.18)	2.99 (3.04)	7.02 (7.10)	783 (788)
3	W ₂ C ₃₁ H ₂₄ N ₄ O ₉	77	35.33 (38.61)	2.45 (2.48)	5.29 (5.80)	959 (964)
4	Cr ₂ C ₃₂ H ₂₈ N ₄ O ₁₀	76	49.67 (52.41)	3.78 (3.82)	7.07 (7.64)	728 (732)
5	Mo ₂ C ₃₃ H ₂₈ N ₄ O ₁₁	78	43.99 (46.67)	3.26 (3.30)	6.27 (6.60)	843 (848)
6	W ₂ C ₃₃ H ₂₈ N ₄ O ₁₁	80	37.42 (38.66)	2.69 (2.73)	5.22 (5.46)	1019 (1024)

Table 2: Selected I.R. spectral bands (cm⁻¹) of H₂L and H₂L' and (1-6)

Complexes	ν (CO)	ν (C=N)	Intramolecular ν		
			(O-H) hydrogen bonding	ν (OH)	ν (phen C-O)
H ₂ L	-	1607 s	2880 w	3415 m	1280 m
H ₂ L'	-	1608 s	2869 w	3440 m	1289 w
1	1712 s	1610 s	2885 w	3408 s	1286 w
2	1966 s, 1710 m	1610 s	2885 w	3383 w	1296 w
3	1960 s, 1711 m	1613 s	2876 w	3422 s	1303 w
4	1710 s	1610 s	2877 w	3419 s	1293 w
5	1962 s, 1718 m	1612 s	2872 w	3431 m	1285 w
6	1969 s, 1717 m	1611 s	2877 w	3414 s	1289 w

RESULTS AND DISCUSSION

Since the quadridentate H_2L and H_2L' ligands are strong electron donors, the imine and phenol groups will assure strong binding to the metal as found in quadridentate salen type complexes¹⁶⁻¹⁹.

Recently, photogeneration of $M(CO)_5$ from $M(CO)_6$ ($M = Cr, Mo, W$) has been extensively studied²⁰⁻²⁵. These 16-electron containing $M(CO)_5$ fragment react quickly with any available donor. The photochemical reaction of $M(CO)_5THF$ ($M = Cr, Mo, W$) with quadridentate Schiff bases H_2L and H_2L' proceed in this expected manner to yield hitherto unknown series of complexes **1-6**. The synthetic routes shown in Fig. 2 can be suggested for the formation of complexes **1-6**. Irradiation of $M(CO)_5THF$ ($M = Cr, Mo, W$) in the presence of 2-hydroxy benzamido-2-hydroxybenzaladimine (H_2L) or 2-hydroxybenzamido-2-hydroxy-3-methoxybenzaladimine (H_2L') resulted in conversion into new $[(\mu-CO)_2Cr_2(\eta^4-H_2L)_2]$, **1**; $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L)_2]$, [$M = Mo$; **2**, W ; **3**]; $[(\mu-CO)_2Cr_2(\eta^4-H_2L')_2]$, **4** and $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L')_2]$, [$M = Mo$; **5**, W ; **6**], which are isolated and characterized by elemental analyses and IR spectra.

The analytical results and some physical properties of the complexes **1-6** are given in Table 1. The stoichiometries of the ligands and their complexes were confirmed by their elemental analyses. The complexes are air stable and soluble in all chlorinated solvents. The absorption frequencies of all $[(\mu-CO)_2Cr_2(\eta^4-H_2L)_2]$, **1**; $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L)_2]$, [$M = Mo$; **2**, W ; **3**]; $[(\mu-CO)_2Cr_2(\eta^4-H_2L')_2]$, **4** and $[(\mu-CO)M_2(CO)_2(\eta^4-H_2L')_2]$, [$M = Mo$; **5**, W ; **6**] complexes are enlisted in Table 2.

The IR spectra of **1** and **4** exhibit one prominent band at 1712 and 1710 cm^{-1} , respectively in the CO stretching vibrational region. One band ν (CO) pattern at this region clearly indicates the presence of two bridging CO groups, which are at similar positions. The IR spectrum of **2** contains two bands at 1966 cm^{-1} and 1710 cm^{-1} in the CO stretching vibrational region. The band at 1710 cm^{-1} indicates the presence of a bridging CO group between the metal atoms, the band at 1966 cm^{-1} belongs to two terminal CO groups. Terminal CO groups and Schiff base ligand in **2** are at trans-position with each other. As indicated²⁷ in, $trans-[(\mu-CO)_2Fe_2(CO)_2cp_2]$, has similar structure with **2**, possessed two CO bands at 1962 cm^{-1} and 1794 cm^{-1} like **2**. In addition, some literature explains that $[(\mu-CO)Fe_2(CO)_2cp_2]$, which has one bridging CO group and two terminal CO group at cis-positions, indicate three bands in the CO stretching vibrational region. The situation supports that the coordination of CO and Schiff base ligands to the metal centers is at trans- positions rather than cis- position. The IR spectra of **3**, **5** and **6** contain essentially the same ν (CO)

absorption pattern as observed for **2**. These vibrational modes shift to lower wave numbers, when compared with these of $M(CO)_6$ and $M(CO)_5$ THF ($M = Cr, Mo, W$).

The IR spectra of the complexes **1-6** showed the characteristic band of H_2L and H_2L' with the appropriate shifts due to complex formation. The bands in the IR spectra of the Schiff bases H_2L and H_2L' at 2880 cm^{-1} and 2869 cm^{-1} , respectively are assigned to the stretch of the intra molecular hydrogen bonded $-OH$ ^{1,16}. The bands appeared and displayed shifts considerably in the IR spectra of the complexes **1-6**. However, appearance of the intramolecular hydrogen bonded $-OH$ bands, the broad and medium $\nu(OH)$ bands occurring 3415 cm^{-1} and 3440 cm^{-1} in the IR spectra of H_2L and H_2L' , respectively, show considerable shifts in the IR spectra of complexes. The strong bands at nearly 1607 cm^{-1} in the IR spectra of free H_2L and H_2L' belong to the $C=N$ stretching vibration^{1,16}. This band show shifts in compounds **1-6**, showing that H_2L and H_2L' ligands coordinate to the metal via the imine ($HC=N$) nitrogen donor atom and donation of the a lone pair of nitrogen atoms with almost no involvement of $C=N$ π -bonds⁶. The bands observed at 1280 cm^{-1} and 1289 cm^{-1} related to phenolic $C-O$ stretching vibration in the IR spectra of H_2L and H_2L' are found in the region $1286-1303\text{ cm}^{-1}$ and $1285-1293\text{ cm}^{-1}$ in the IR spectra of complexes. These changes suggest that the orthro hydroxyl ($o-OH$) groups of H_2L and H_2L' moieties have taken part in complex formation without elimination of hydrogen atoms from the OH groups, which were also confirmed by the appearance of the new band in the spectra of the metal complex at $515-578\text{ cm}^{-1}$ and $401-440\text{ cm}^{-1}$ ascribed to the $M-O$ and $M-N$ vibrations^{1,16}. These were not seen in the spectra of the ligands. In addition, magnetic susceptibility measurement showed that **1-6** complexes were diamagnetic. Since these complexes have $M(0)$ [$M = Cr, Mo, W$] with a low spin d^6 configuration. Such diamagnetism might arise from further splitting of the d-orbital in the low symmetry complexes¹. i.e. $d_{xy}^2, d_{xz}^2, d_{yz}^2, d(x^2-y^2)^0, dz^2^0$.

In homoleptic binuclear metal carbonyls, the pair of metal atoms provides two fewer electrons for bonding, so that additional ligands are required for each metal atom to attain the favored 18-electron noble gas configuration²⁹. According to the 18-electron rule, two metal atoms must interact with each other to stabilize the complexes **1-6**. $Cr=Cr$ double bond is required to give each chromium atom the favored 18-electron rare gas configuration, if the single terminal CO group is a normal two electron donor and bridging CO group is a one-electron donor in **1** and **4**. In **2,3,5** and **6** complexes, a single bond between M atoms ($M = Mo, W$) is enough to reach 18-electrons rare gas configuration.

CONCLUSION

IR spectra of the complexes represent that the H_2L and H_2L' ligands coordinate to the

metal atoms via both azomethine's nitrogen and oxygen donor atoms, behaving like quadridentate neutral ligand. Thus, C=N stretching vibration and the stretch of the intramolecular hydrogen bonded –OH in the IR spectra of the complexes exhibit shifts compared with that of ligands. One and two prominent carbonyl bands in the CO stretching vibrational region belonging to two bridging and one bridging–two terminal carbonyl complexes are displayed in **1**, **4** and **2**, **3**, **5** and **6** are in good agreement with the expected structures of **1–6**.

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REFERENCES

1. S. Karahan, Pelinkose, and E. S. H. Temel, Synth. React. in Inorg., Metal-Org. Nano-Metal Chem., **38**, 422-427 (2008).
2. N. P. Buu-Hoi and N. D. Xuong, p-Cyclopentylacetophenone and its Derivatives, J. Org. Chem., **23**, 39 (1958).
3. J. Russel and H. J. Clark, The Constitution of Natural Tannins, VI. Coloring Matters Derived from 2,5-Dihydroxyacetophenone, J. Am. Chem. Soc., **61**, 3651 (1939).
4. K. Syam Sunder, Chalcones as Inorganic Analytical Reagents, Part II, Amperometric Estimation of Copper with 2',3',4'-Trihydroxy Chalcone, Proc. Indian Acad. Sci., **4**, 241 (1964).
5. E. Subasi, H. Temel, O. S. Senturk and F. Ugur, Photochemical Reactions of Metal Carbonyls [M(CO)₆ (M = Cr, Mo; W)] with N,N' – bis (salicylidene) -1,2-bis-(o-aminophenoxy) ethane. J. Coord. Chem., **59**, 1807-1811 (2006).
6. J. Chakraborty and R. N. Patel, Copper, Cobalt – and Zinc (II) complexes with Monofunctional Bidentate Schiff Base and Monodentate Neutral Ligands, J. Indian Chem. Soc., **73**, 191 (1996).
7. R. Klement, F. Stock, H. Ellias, H. Paulus, P. Pelikan, M. Valko and M. Mazur, Copper (II) Complexes with Derivatives of Salen and Tetra-hydrosalen: A

- Spectroscopic, Electrochemical and Structural Study, *Polyhedron*, **18**, 3617-3628 (1999).
8. D. Chen and A. E. Martell, Dioxygen Affinities of Synthetic Cobalt-Schiff Base Complexes, *Inorg. Chem.*, **26**, 1026-1030 (1987).
 9. J. Zhao, B. Zhao, J. Liu, W. Xu and Z. Wang. Spectroscopy Study on the Photochromism of Schiff Bases. N, N'-bis (Salicylidene) -1,2- diaminoethane and N, N'-Bis (salicylidene)-1, 6-hexanediamine, *Spectrochim. Acta*, **57 A**, 149 (2001).
 10. W. J. Sawodny and M. Riederer, Addition Compounds with Polymeric Chromium (II) – Schiff Base Complexes, *Angew. Chem. Int. Edn. Engl.*, **16**, 859 (1977).
 11. M. Z. Zgierski and A. J. Grabowska. Theoretical Approach to Photochromism of Aromatic Schiff Bases. A Minimal Chromophore Salicylidene Methylamine, *J. Chem. Phys.*, **113**, 7845-7852 (2000).
 12. Amar Srivastava and A. K. Shrimal, Schiff Base Derivatives of Tungsten Carbonyl, *Indian J. Chem.*, **41A**, 785-790 (2002).
 13. W. Kaim and S. Kohlmann, Four Bridging Bis Chelate Ligands with Very Low Lying Orbitals. MO Perturbation Calculations, Electrochemistry and Spectroscopy of Mononuclear and Binuclear Group-6 Metal Carbonyl Complexes, *Inorg. Chem.*, **26**, 68-77 (1987).
 14. B. M. Trost and M. Lautens, On the Stereo- and Regioselectivity of Molybdenum Catalysed Allylic Alkylations. Stereocontrolled Approach to Quarter Many Carbons and Tandem Alkylation- Cycloaddition, *J. Am. Chem. Soc.*, **50**, 105, 3343-3344 (1983).
 15. S. G. Shankarwar, A. C. Sankarwar and T. K. Chondhekar, *Acta Ciencia Indica*, **XXXIV C**, 219-222 (2008).
 16. H. Temel, S. Ilhan, M. Sekerei and R. Ziyadanoullari. The Synthesis and Spectral Characterization of new Cu (II), Ni (II), Co (III) and Zn (II) Complexes with Schiff Base, *Spect. Lett.*, **35**, 219-228 (2002).
 17. H. Tamel and M. Sekerci, Novel Complexes of Manganese (III), Cobalt (II), Copper (II), and Zinc (II) with Schiff Base derived from 1,2- Bis (2-aminophenoxy-ethane and Salicylaldehyde, *Synth. React. Inorg. Met. Org. Chem.*, **31**, 849-857 (2001).
 18. M. R. Bermejo, A. Sousa, A. Garcia-Deibe, M. Maneiro, M. Sanmartin and J. Fondo, Synthesis and Characterization of New Manganese (III) Complexes with Asymmetrical ONSN Schiff Bases, *Polyhedron*, **18**, 511-518 (1999).

19. H. Temel, U. Cakir, H. I. Ugras and M. Sekerci, The Synthesis, Characterization and Conductance Studies of New Cu(II), Ni(II) and Zn(II) Complexes with the Schiff Base derived from 1, 2-Bis-(o-aminophenoxy)ethane and Salicylaldehyde, *J. Coord. Chem.*, **56**, 943-951 (2003).
20. H. Temel, S. Irhan and M. Sekerci, Synthesis and Characterization of a New Bidentate Schiff Base and its Transition Metal Complexes, *Synth. React. Inorg. Met. Org. Chem.*, **32**, 1625-1634 (2002).
21. O. S. Senturk, H. A. Shekkel, B. T. Strenberg, K. A. Udachin, S. Sert, F. Ugur and U. Ozdemir, Photochemical Reaction of $\text{Re}(\text{CO})_5\text{Br}$ with Tetraalkyl diphosphine disulfides ($\text{R} = \text{Me}, \text{Et}, \text{Pr-n}, \text{Bu-n}, \text{Ph}$) and the Crystal Structure of $[\text{ReBr}(\text{CO})_3(\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2)]$, *Polyhedron*, **22**, 1659-1664 (2003).
22. E. Subasi, O. S. Senturk and F. Ugur, Photochemical Reactions of $\text{Re}(\text{CO})_5\text{Br}$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, \text{dppm}; 2, \text{dppe}; 3, \text{dppp}$), *Transit. Met. Chem.*, **29**, 16-18 (2004).
23. E. Subasi, O. S. Senturk and F. Ugur, Photochemical Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$ with $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$ [$n = 1, \text{dppm}(\text{S})_2; 2, \text{dippe}(\text{S})_2; 3, \text{dppp}(\text{S})_2$], *Transit. Met. Chem.*, **29**, 649-652 (2004).
24. E. Subasi, O. S. Senturk and F. Ugur, Photochemical Reactions of $\text{Re}(\text{CO})_5\text{Br}$ with $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$ ($n = 1, 2, 3$), *Z. Naturforsch.*, **59b**, 836-838 (2004).
25. S. Sert, O. S. Senturk and F. Sarikahya. Photochemical Reactions of Chromium Hexacarbonyl with Tetraalkyl diposphine disulphides, *Transit. Met. Chem.*, **27**, 700-703 (2002).
26. S. Sert, O. S. Senturk and F. Sarikahya, Photochemical Reaction of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with $\text{Ph}_2\text{P}(\text{S})\text{P}(\text{S})\text{Ph}_2$, *Transit Met. Chem.*, **28**, 133-136 (2003).
27. F. Sarikahya and O. S. Senturk, Photochemical Synthesis of Metal Carbonyl Complexes of Tetraalkyl diphosphine disulphides, $[\text{M}_2(\text{CO})_{10}(\text{u-R}_2\text{P}(\text{S})\text{P}(\text{S})\text{R}_2)]$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Me}, \text{Et}, \text{n-Pr}, \text{n-Bu}$), *Synth. React. Inorg. Met.*, **31**, 1843-1851 (2001).
28. H. Wang, Y. Xie, R. B. King and I. I. F. Schaefer, Unsaturation in Binuclear Cyclopentadienyl Iron Carbonyls, *Inorg. Chem.*, **45**, 3391-5629 (2006).
29. S. Li, N. A. Richardson, R. B. King and H. F. Schaefer, Chromium-Chromium Multiple Bonding in $\text{Cr}_2(\text{CO})_9$, *J. Phys. Chem.*, **A 107**, 101-118 (2003).

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