

SYNTHESIS AND CHARACTERIZATION OF FEW IRON, RHENIUM AND MANGANESE COMPLEXES CONTAINING NITROGEN, PHOSPHOROUS AND SULFUR DONOR LIGANDS

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Abstract

Reaction of $[\text{Mn}_2(\text{CO})_8(\text{NCMe})_2]$ and $[\text{Re}_2(\text{CO})_8(\text{NCMe})_2]$ with triphenyltinpyridine-2-thione (pySSnPh_3) furnishes di-nuclear complexes $[\text{Mn}_2(\mu_3\text{-}\kappa^3\text{-pyS})_2(\text{CO})_6]$ (1), $[\text{Re}_2(\mu_3\text{-}\kappa^3\text{-pyS})_2(\text{CO})_6]$ (2) and mono-nuclear complex $[\text{Mn}(\text{CO})_3(\text{S})_2(\text{SnPh}_3)]$ (3), where pyridine-2-thiolato ligand added with 1 and 2 as a bidentate fashion. Another reaction of $[\text{Re}_2(\text{CO})_{10}]$ with $[\text{PhSSPh}]$ and 2-methyl-pyrazine forms cubic complex $[\text{Re}_4(\text{CO})_{12}(\mu_3\text{-}\kappa^3\text{-SPh})_4]$ (4) and reaction of $\text{Fe}_2(\text{CO})_9$ with bis(diphenylphosphino)methane (dppm) gives $[\text{Fe}(\text{CO})_4(\kappa^1\text{-dppm})]$ (5). The molecular structures of all these complexes have been determined by IR, ¹H NMR, ³¹P NMR spectroscopy and mass spectrometry.

Keywords: Manganese, Rhenium, Iron, Pyridine-2-thiol and dppm.

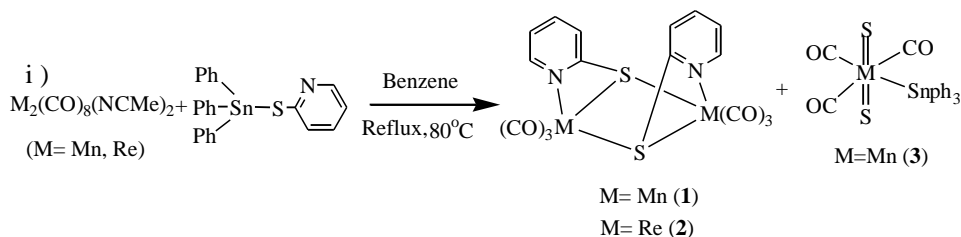
Introduction

The study of the reactivity of nitrogen and sulfur containing small heterocyclic organic molecules towards transition metal carbonyl clusters has attracted considerable interest because such ligands frequently stabilizes the metal cluster framework by serving as chelating or bridging ligands (Brodie, 1986; Au, 1995a and 1995b; Jeannin, 1978) and also due to their potential applicability in modeling hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes (Dilshad, 1999; Hanif, 1999). These reactions are usually accompanied by C—H, N—H, S—H and C—N bonds activation of the heterocyclic ligand and markedly influenced by the structure of the heterocycle as well as the reaction conditions and starting complexes. Several authors have investigated the reactions of thiazole (Azam, 1998a and 1998b), 4-methylthiazole (Azam, 1996), {thiazolidine, thiomorpholine (Hanif, 1999)}, {benzothiazole, benzimidazole-2-thiol (Dilshad, 1999)} and {pyridine-2-thiol, pyrimidine-2-thiol (Kabir, 2000)} with osmium and ruthenium carbonyl clusters and observed that the type of products obtained in these reactions are remarkably influenced by the intrinsic reactivity of the metal carbonyl clusters, the heterocyclic ligands and the reaction conditions. The authors have also investigated the reaction of manganese carbonyl and rhenium carbonyl with pyrimidine-2-thiol (Kabir, 2009) and 6-methylpyridine-2-thione (Deeming and Karim, 1988; Kabir, et. al. 1996). They observed that 6-methylpyridine-2-thione ligand added with metal same fashion like pyridine-2-thiol ligand. The interaction of heterocyclic thiones with transition metals has attracted much attention due to their biochemical significances and their uses as medicinal substances (Katiyar, 2003; Scheit, 1969). Metal complexes and their

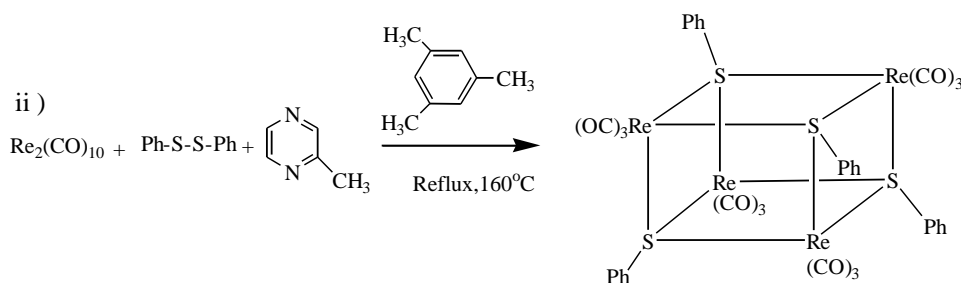
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substitution reactions have been studied extensively by using various ligands e.g. alkynes, phosphines and phosphites, but also a variety of sulfur donor ligands have been employed (Wilkinson, 1982). When catalytic processes are studied, sulfur being one of the foremost catalyst poisons (Rossi, 1990). We have synthesized and characterized some of few similar complexes herein.

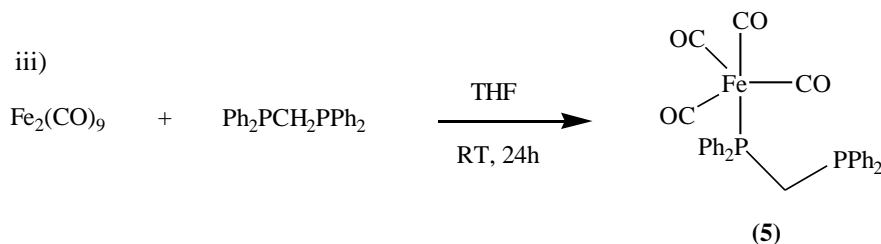
Reaction



Scheme 1



Scheme 2



Experimental

Reaction of [Mn₂(CO)₈(NCMe)₂] with [pyS-SnPh₃]

A benzene solution (30 mL) of [Mn₂(CO)₈(NCMe)₂] (80mg, 0.192 mmol) and [pyS-SnPh₃] (89mg, 0.192 mmol) was stirred at 80°C for 1.5h. The solvent was removed by rotary evaporator and the compounds in residue were separated by preparative TLC on silica gel. Elution with hexane/CH₂Cl₂ (6:4, v/v) developed five bands. The second and fourth band gave unreacted [Mn₂(CO)₈(NCMe)₂] (trace) and [pyS-SnPh₃] (trace). The first band afforded [Mn(CO)₃(S)₂(SnPh₃)] (3), (50mg, 67%) (Scheme 1) as white crystals and the third band afforded [Mn₂(μ₃-κ³-pyS)₂(CO)₆] (1) (25mg, 34%) (Scheme 1) as orange crystals after recrystallization from hexane/CH₂Cl₂ at 4°C. Spectral data for 3:

Anal. Calc. for $C_{27}H_{15}Mn_2O_9Sn$: C, 45.52; H, 2.12%. IR (ν_{CO} , CH_2Cl_2): 2035 s, 2001 (br, vs) cm^{-1} . 1H NMR ($CDCl_3$): δ 7.34 - 7.64 (m, 15 H). MS (FAB): m/z 553 (M^+), 531, 455, 443 (base peak), 355, 311.

Reaction of $[Re_2(CO)_8(NCMe)_2]$ with $[pyS-SnPh_3]$

The benzene solution (30 ml) of $[Re_2(CO)_8(NCMe)_2]$ (80mg, 0.192 mmol) and $[pyS-SnPh_3]$ (54mg, 0.118 mmol) was stirred at 80°C for 12h. After removal of the solvent under reduced pressure, the residue was chromatographed by preparative TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3 v/v) gave six bands. The major band gave the complex $[Re_2(\mu_3-\kappa^3-pyS)_2(CO)_6]$ (2) (37mg, 42.05%) (Scheme 1) as pale yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4°C. The content of the other minor bands were too small for complete characterization. The spectral data for 2: IR (ν_{CO} , CH_2Cl_2): 2037 s, 2020 vs, 1937 m, 1918 (br, s) and 1911 (br, s) cm^{-1} . This complex was synthesized and reported earlier (Deeming., 1988) but our method was different than the reported method. Deeming reported the complex by X-ray diffraction studies only without taking any 1H -NMR and mass spectra.

Reaction of $[Re_2(CO)_{10}]$, $[PhSSPh]$ and 2-methyl-pyrazine in mesitylene

A mesitylene solution (30 mL) of $Re_2(CO)_{10}$ (60mg, 0.085 mmol) with $[PhSSPh]$ (19mg, 0.087 mmol) and 2-methyl-pyrazine was stirred at 160°C for 24h. The solvent was removed under reduced pressure and the compounds in residue were separated by preparative TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3, v/v) developed one band and resulting the isolation of the cluster $[Re_4(\mu_3-\kappa^3-SPh)_4(CO)_{12}]$ (4) (20mg, 30%) (Scheme 2) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4°C. Spectral data for 4: Anal. Calc. for $C_{36}H_{20}Re_4O_{12}S_4$: C, 28.47; H, 1.32%. IR (ν_{CO} , CH_2Cl_2): 2033 vs, and 1946 (br, vs) cm^{-1} .

1H NMR ($CDCl_3$): δ 7.38 (t, 1H), 7.56 (t, 1H), δ 7.82 (d, 1H). Mass spectrum, m/z : $[M^+]=1517, 1349, 1024, 808, 219$ (base peak).

Reaction of $Fe_2(CO)_9$ with Bis(diphenylphosphino) methane

Di-iron nonacarbonyl was first dried in vacua and then 5g (0.0136 mmol) was placed in a round-bottom flask with 3.0 g (0.0078 mmol) of bis(diphenylphosphino)methane. Tetrahydrofuran (100ml) which was dried over molecular sieves, was added under an argon flush. The reaction mixture was stirred at RT for 24h and then chromatographed on 100-200 mesh florisil. Elution with hexane/ CH_2Cl_2 (8:2 v/v) gave two bands. The major band gave the complex $[Fe(CO)_4(\kappa^1-dppm)]$ (5) (3100mg, 56%) (Scheme 3) as pale yellow crystals after recrystallization from hexane/ CH_2Cl_2 at 4°C. Spectral data for 5: Anal. Calc. for $C_{28}H_{20}FeO_4P_2$: C, 62.46; H, 3.75%. IR (ν_{CO} , CH_2Cl_2): 2048 vs, 1973 (br, s) and 1938 (br, vs) cm^{-1} . 1H NMR ($CDCl_3$): δ 7.18-7.34 (m, 20H), δ 3-3.6 (m, 2H) and $^{31}P\{^1H\}$ NMR($CDCl_3$): δ -26 (d, J =60.42 Hz) and δ - 28.53 (d, J = 40.98 Hz). Mass spectra was not taken.

Results and Discussion

Reaction of $[Mn_2(CO)_8(NCMe)_2]$ with $[pyS-SnPh_3]$: Formation of mono and di-manganese complexes

The reaction of $[Mn_2(CO)_8(NCMe)_2]$ with $[pyS-SnPh_3]$ in benzene at 80°C, followed by usual workup and preparative chromatographic separation, afforded two manganese

complexes $[\text{Mn}(\text{CO})_3(\text{S})_2(\text{SnPh}_3)]$ (**3**) (50mg, 67%) and $[\text{Mn}_2(\mu_3\text{-}\kappa^3\text{-pyS})_2(\text{CO})_6]$ (**1**) (25mg, 34%) (Scheme 1). Complex **1** had been reported previously (Kabir *et al.*, 1996). We have characterized complex **1** by comparing its IR spectrum with the reported one but our present synthetic route was completely different and gave another new complex **3** which has been characterized by elemental analysis, IR, ^1H NMR and mass spectral data. The infrared spectrum of compound **3** displays only two absorption bands at 2001 (s) and 2095 (br, vs) cm^{-1} indicating that all the carbonyl groups present in the molecule are terminally bonded while the mass spectrum exhibits a parent molecular ion peak at m/z : 553 consistent with our proposed structure. The ^1H NMR spectrum shows two multiplets in the aromatic region at δ 7.34 to 7.64 in 2:3 intensity ratio which is attributable to the phenyl protons of the triphenyltin ligand.

Reaction of $[\text{Re}_2(\text{CO})_8(\text{NCMe})_2]$ with $[\text{pyS-SnPh}_3]$: Formation of di-rhenium complex

The reaction of $[\text{Re}_2(\text{CO})_8(\text{NCMe})_2]$ with $[\text{pyS-SnPh}_3]$ in benzene at 80°C , followed by usual workup and preparative chromatographic separation, afforded one rhenium complex $[\text{Re}_2(\mu_3\text{-}\kappa^3\text{-pyS})_2(\text{CO})_6]$ (**2**) (37mg, 42.05%) (Scheme 1). Complex **2** had been reported previously (Deeming *et al.*, 1988) and we characterized by comparing its IR spectrum with Deeming reported one but our synthetic route was completely different. We also found similar band like **3** in preparative TLC (Thinlayer Chromatography) but not characterized due to poor amount.

Reaction of $[\text{Re}_2(\text{CO})_{10}]$, $[\text{PhSSPh}]$ and 2-methyl-pyrazine in mesitylene: Formation of a cubic complex

One pot reaction of $[\text{Re}_2(\text{CO})_{10}]$, $[\text{PhSSPh}]$ and 2-methyl-pyrazine in refluxing mesitylene at 160°C , followed by usual work up and chromatographic separation as mentioned in the experimental section, resulted in the isolation of the complex $[\text{Re}_4(\text{CO})_{12}(\mu_3\text{-}\kappa^3\text{-SPh})_4]$ (**4**) (20mg, 30%) (Scheme 2). The infrared spectrum of complex $[\text{Re}_4(\text{CO})_{12}(\mu_3\text{-}\kappa^3\text{-SPh})_4]$ exhibits two absorption bands at 2033 (vs) and 1946 (br, s) cm^{-1} indicating that all the carbonyl ligands are terminally bonded. The ^1H NMR spectrum shows only aromatic resonance which ruled out the incorporation of 2-methyl-pyrazine in the complex. In aromatic region one para hydrogen of benzene ring shows triplet at δ 7.38. Two equivalent meta and ortho hydrogen shows triplet and doublet at δ 7.56, 7.85 respectively. On the other hand the mass spectrum of **4** displays a parent molecular ion peak at m/z : $[\text{M}^+] = 1517$ which is in accord with our proposed structure. It is also noted that the peak 1349 and 1024 arise due to loss of 6CO and $(4\text{Sph}+2\text{CO})$ respectively. The base peak 219 arises only for Re-S fragment in mass spectrometry.

Reaction of $\text{Fe}_2(\text{CO})_9$ with bis(diphenylphosphino)methane: Formation of mono nuclear complex

Stirring $[\text{Fe}_2(\text{CO})_9]$ and $[\text{pySH}]$ in THF (Tetrahydrofuran) for 24h at room temperature followed by usual workup and chromatographic separation as mentioned in the experimental section, resulted in the isolation of $[\text{Fe}(\text{CO})_4(\kappa^1\text{-dppm})]$ (**5**) as pale yellow crystals (3100mg, 56%) (Scheme 3). It was assumed that first form the complex $[\text{Fe}_2(\text{CO})_7(\text{Ph}_2\text{P})_2\text{CH}_2]$ (Cotton, 1974) and later it decomposed to **5**. The twenty phenyl hydrogen resonance in the usual aromatic region at δ 7.18-7.34 and aliphatic two hydrogens shows resonance at δ 3-3.6. In ^{31}P NMR shows two doublet at δ -26 (J = 60.42 Hz) and δ -28.53 (J = 40.98 Hz) which is attributable for one phosphorus coordination. (if two phosphorus coordinated shows one doublet).

Conclusion

In summary, the reaction of [pySSnPh₃] with [M₂(CO)₁₀(NCMe)₂] afforded the expected mononuclear complex [Mn(CO)₃(S)₂(SnPh₃)] (**3**) together with known complexes [Mn₂(μ₃-κ³-pyS)₂(CO)₆] (**1**) and [Re₂(μ₃-κ³-pyS)₂(CO)₆] (**2**). This reaction is most interesting due to the formation of the complex **3** by displacement of sulfur from the ligand. The formation of a cubic complex [Re₄(CO)₁₂(μ₃-κ³-Sph)₄] (**4**) is also more interesting. The formation of iron complex is very sensitive due to their instability. The formation of the complex [Fe(CO)₄(κ¹-dppm)] (**5**) from [Fe₂(CO)₇(Ph₂P)₂CH₂] (Cotton, 1974) is due to same cause.

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References

- Au, Y. K., K. K. Cheung and W. T. Wong, (1995a). Synthesis and structural characterization of ruthenium and osmium carbonyl clusters containing 4,6-dimethylpyrimidine-2-thione, *Inorg. Chem. Acta.*, **228**: 267-275.
- Au, Y. K., K. K. Cheung and W. T. Wong, (1995b). Synthesis, structural characterization and thermal reactivities of osmium carbonyl clusters containing 4,6-dimethylpyrimidine-2-thione, *J. Chem. Soc., Dalton Trans.*, 1047-1057.
- Azam, K. A., R. Dilshad, S. E. Kabir, K. Khatoon, L. Nessa, M. M. Rahman, E. Rosenberg, M. B. Hursthouse, K. M. A. Malik and A. J. Deeming, (1996). Triosmium and triruthenium clusters containing the 4-methylthiazolide ligand: crystal structures of [Os₃(μ-H)(CO)₁₀(μ-2,3-η²-C=NCMe=CHS)], [Os₃(μ-H)(CO)₉(μ-2,3-η²-C=NCMe=CHS)(PPh₃)] and [Os₃(μ-H)(CO)₈(μ-2,3-η²-C=NCMe=CHS)(PPh₃)₂], *J. Chem. Soc., Dalton Trans.*, 1731-1739.
- Azam K. A., M. B. Hursthouse, S. E. Kabir, K. M. A. Malik, M. Tesmer and H. Vahrenkamp, (1998a). A novel pentaruthenium cluster containing three thiazole derived ligands; X-ray structure of [(Ru₅(CO)₉(μ-H)(μ⁵-η⁵-HC=NC=CHS)Ru₂(CO)₄(μ-H)(η¹-HC(η¹-HC=NCH=CHS)=NCH=CHS)(μ-2,3-η³-C(μ-2,3-η³-C=NCH=CHS)=NCH=CHS)], *Inorg. Chem. Commun.*, **1** (10): 402-404.
- Azam, K. A., S. A. Hussain, S. E. Kabir, M. M. Rahman, M. B. Hursthouse, K. M. A. Malik and E. Rosenberg, (1998b). Triosmium clusters containing thiazolide ligand : crystal structures of (MU-H)OS₃(CO)₁₀(MU-3,4-ETA₂-HC=NC=CHS) and (MU-H)OS₃(CO)₉(MU-3,4-ETA₂-HC=NC=CHS)(PPh₃), *J. Organomet. Chem.*, **559**: 81-89.
- Brodie, A. M., H. D. Holden, J. Lewis and M. J. Taylor, (1986). The reaction of [Os₃(CO)₁₀(MeCN)₂], with heterocyclic thioamides. The crystal and molecular structure of [Os₃(μ-H)(CO)₁₀(μ-SC=NCH₂CH₂S)], *J. Chem. Soc., Dalton Trans.*, 633-639.
- Dilshad, R., K. M. Hanif, M. B. Hursthouse, S. E. Kabir, K. M. A. Malik and E. Rosenberg, (1999). Triruthenium clusters derived from the reactions of [Ru₃(CO)₁₂] with benzothiazole, pyrimidine-2-thione and benzimidazole-2-thione; X-ray structures of [Ru₃(μ-H)(μ-2,3-η²-NSC₇H₄)(CO)₁₀] and [Ru₃(μ-H)(μ₃-η²-SN₂C₄H₃)(CO)₉], *J. Organomet. Chem.*, **585**: 100-105.
- Deeming, A. J. and M. Karim, (1988). A new type of pyridine-2-thionato bridge: x-ray crystal structure of the complex [Re₂(MepyS)₂(CO)₆] where MepyS is the 6-methylpyridine-2-thionato ligand, *Polyhedron.*, **7**: 1401-1403.

- Ghosh, S., F. K. Camellia, K. Fatema, M. I. Hossain, M. R. Al-Mamun, G. M. G. Hossain, G. Hogarth and S. E. Kabir, (2011). Centrosymmetric $[\text{Mn}_2(\text{CO})_6(\mu\text{-thpymS})_2]$ (thpymS-tetrahydropyrimidine-2-thionato) as a synthon to mixed-metal clusters, *J. Organomet. Chem.*, **695**: 2935-2942.
- Hanif, K. M., M. B. Hursthouse, S. E. Kabir, K. M. A. Malik and E. Rosenberg, (1999). Ring-opening reactions of thiomorpholine and thiazolidine by $[\text{Ru}_3(\text{CO})_{12}]$: crystal structures of $[\text{Ru}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-SCH}_2\text{CH}_2\text{NH}_2)(\text{CO})_9]$ and $[\text{Ru}_2(\mu\text{-}\eta^3\text{-SCH}_2\text{CH}_2\text{NHCH}_2)(\text{CO})_6]$, *J. Organomet. Chem.*, **580**: 60-65.
- Jeannin, S., Y. Jeannin and G. Lavigne, (1978). (Structural study of transition-metal hydride complexes in relation to corrosion inhibition: crystal and molecular structure of $\text{Ru}_3\text{H}(\text{CO})_{10}(\text{SCH}_2\text{COOH})$ and $\text{Ru}_3\text{H}(\text{CO})_9(\text{C}_7\text{H}_4\text{NS}_2)$, *Inorg. Chem.*, **17(8)**: 2103-10.
- Kabir, S. E., K. M. A. Malik, E. Molla and M. A. Mottalib, (2000). Reactivity of $[(\mu\text{-H})\text{Os}_3(\text{CO})_8\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$ with organic heterothiols; X-ray structures of $[\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_8(\eta^2\text{-pyS})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$ and $[\text{Os}_3(\text{CO})_8(\mu\text{-}\eta^2\text{-pyS})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$, *J. Organomet. Chem.*, **616**: 157-164.
- Kabir, S. E., J. Alam, S. Ghosh, K. Kundu, G. Hogarth, D. A. Tocher, G. M. G. Hossain and H. W. Roesky, (2009). Synthesis, structure and reactivity of tetranuclear square-type complexes of rhenium and manganese bearing pyrimidine-2-thiolate (pymS) ligands: versatile and efficient precursors for mono- and polynuclear compounds containing $\text{M}(\text{CO})_3$ fragments, *Dalton Trans.*, 4458-4467.
- Kabir, S. E., M. M. Karim, K. Kundu, S. M. B. Ullah and K. I. Hardcastle, (1996). Some pyridine-2-thiolato and 6-methylpyridine-2-thiolato complexes of manganese: crystal structure of $[\text{Mn}_2(\mu\text{-pyS})_2(\text{CO})_6]$, *J. Organomet. Chem.*, **517**: 155-159.
- Katiyar, D., V. K. Tiwari, R. P. Tripathi, A. Srivastava, V. Chaturvedi, R. Srivastava, B. S. Srivastava, (2003). Synthesis and antimycobacterial activity of 3,5-disubstituted thiadiazine thiones, *Bioorg. Med. Chem.*, **11(20)**: 4369-4375.
- Rossi, S., J. Pursiainen, M. Ahlgren and T. A. Pakkanen, (1990). Dimethylsulfide Substituted Mixed Metal Clusters: Synthesis, Structure and Characterization of $\text{HRuCo}_3(\text{CO})_{11}(\text{SMe}_2)$ and $[\text{HRuRh}_3(\text{CO})_9]_2[\text{SMe}_2]_3$, *Organometallics*, **9**: 475-480.
- Scheit, K. H., E. Gartner, (1969). To study the biological activity of few new metal carbonyl complexes, *Biochim. Biophys. Acta.*, **183**: 10-18.
- Wilkinson, G., F. G. A. Stone and E. W. Abel, (1982). *Comprehensive Organometallic Chemistry*, Pergamon: Oxford, England.