

CARBON-HYDROGEN BOND ACTIVATION OF PHENYLDI(2-THIENYL)PHOSPHINE AT A TRIRUTHENIUM CLUSTER CENTER

SHAHED RANA, SHISHIR GHOSH AND SHARIFF E. KABIR*

Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh

Abstract

Ketyl-initiated reaction between $\text{Ru}_3(\text{CO})_{12}$ and phenyldi(2-thienyl)phosphine (PhPTh_2) furnished simple phosphine-substituted triruthenium clusters $[\text{Ru}_3(\text{CO})_{10}(\text{PhPTh}_2)_2]$ **1** and $[\text{Ru}_3(\text{CO})_9(\text{PhPTh}_2)_3]$ **2**. Heating **1** in boiling benzene afforded $[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-PhThP}(\text{C}_4\text{H}_2\text{S})\}(\text{PhPTh}_2)]$ **3** by carbon-hydrogen bond cleavage of a coordinated thienylphosphine ligand. All three new clusters have been characterized by elemental analysis, IR and NMR spectroscopic data.

Introduction

The organometallic chemistry of thiophene is stimulated by the necessity to understand the mechanisms of commercial catalytic hydrodesulfurization reactions.¹⁻⁴ Thiophene and its benzoderivatives normally do not bind strongly with transition metals which is a major drawback to study their behaviors on metal surface. In order to circumvent this problem thienylphosphine has been employed to bring the thiophenes into the coordination sphere of transition metals through the phosphine moiety of the ligand.

This new strategy facilitates the study of thiophenes and its benzoderivatives from the point of view of the hydrodesulfurization process using different metal systems especially by low-valent transition metal clusters.⁵⁻¹⁷ In this context, the reactivity of thienylphosphines with trisium and triruthenium clusters has been thoroughly examined in recent years.¹⁰⁻¹⁷ The first report in this area was by Vahrenkamp *et al.* in 1995 who documented the reaction of $\text{Ru}_3(\text{CO})_{12}$ with tri(2-thienyl)phosphine from which two simple tertiary phosphine substituted products $[\text{Ru}_3(\text{CO})_{10}(\text{PTh}_3)_2]$ and *trans*- $[\text{Ru}(\text{CO})_3(\text{PTh}_3)_2]$ had been isolated in low yields.¹⁰ Later on Deeming *et al.* reported the reactivity of diphenyl(2-thienyl)phosphine with $\text{Ru}_3(\text{CO})_{12}$ and we demonstrated the reactivity of tri(2-thienyl)phosphine with $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ {dppm = bis(diphenylphosphino)methane}.¹¹⁻¹² A worth of interesting reactivity pattern and structural features were obtained from those studies such as carbon-hydrogen and carbon-phosphorous bond cleavage leading to cyclometalated $\mu_3\text{-R}_2\text{P}(\text{C}_4\text{H}_2\text{S})$ (R = Ph, Th) and μ_4 -thiophyne ligands as well as carbon-sulfur bond cleavage leading to thiophene ring opening required for desulfurization. The reactions of thienylphosphines with trisium clusters also lead to the formation of both simple substitution and metalated product which were demonstrated by Nordlander and our research group.¹³⁻¹⁵ As part of our work on the reactivity of thienylphosphines with trimetallic clusters, we have studied the reactivity of phenyldi(2-thienyl)phosphine (PhPTh_2) with $\text{Ru}_3(\text{CO})_{12}$, the results of which are described herein.

*Author for Correspondence; e-mail: skabir_ju@yahoo.com

Experimental

Unless otherwise noted all manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Reagent grade solvents were dried using appropriate drying agents and distilled by standard methods prior to use. Preparative thin-layer chromatography (TLC) plates were prepared with silica gel GF254 (type 60, E. Merck). Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on Varian Unity Plus 500 and Bruker DPX 400 instruments. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. $\text{Ru}_3(\text{CO})_{12}$ was purchased from Strem Chemical Inc. and used without further purification.

Reaction of $\text{Ru}_3(\text{CO})_{12}$ with PhPTh_2

A dry, nitrogen flashed, 100 mL, two necked round bottom flask was charged with $\text{Ru}_3(\text{CO})_{12}$ (200 mg, 0.313 mmol), PhPTh_2 (172 mg, 0.627 mmol), freshly distilled THF (40 mL) and a magnetic stirrer and the resultant mixture was warmed to 40°C for complete dissolution of $\text{Ru}_3(\text{CO})_{12}$. A solution of sodium benzophenone ketyl catalyst (*ca.* 5 drops) was added to this solution with the aid of a syringe. The initial red solution became dark instantaneously. The reaction mixture was stirred for another 15 min at room temperature while the consumption of all the $\text{Ru}_3(\text{CO})_{12}$ was confirmed by analytical TLC. The solvent was removed by rotary evaporation under reduced pressure and the residue separated by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (3:1, v/v) developed two bands which yielded the following compounds in order of elution: $[\text{Ru}_3(\text{CO})_{10}(\text{PhPTh}_2)_2]$ **1** (160 mg, 45%) as deep red crystals and $[\text{Ru}_3(\text{CO})_9(\text{PhPTh}_2)_3]$ **2** (41 mg, 10%) as orange crystals after recrystallization from hexane/ CH_2Cl_2 at 4°C. Spectral data for **1**: Anal. Calcd. for $\text{C}_{38}\text{H}_{22}\text{O}_{10}\text{P}_2\text{Ru}_3\text{S}_4$: C, 40.32; H, 1.96. Found: C, 40.87; H, 2.03%. IR (CO , CH_2Cl_2): 2083 m, 2054 vs, 2015 s, 2000 vs, br cm^{-1} ; ^1H NMR (CDCl_3): 7.62 (m, 4H), 7.46 (m, 12H), 7.16 (m, 6H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 10.5 (s); MS (FAB): m/z 1131 (M^+). Spectral data for **2**: Anal. Calcd. for $\text{C}_{51}\text{H}_{33}\text{O}_9\text{P}_3\text{Ru}_3\text{S}_6$: C, 44.45; H, 2.42. Found: C, 44.97; H, 2.48%. IR (CO , CH_2Cl_2): 2062 m, 2002 vs, 1988 vs, 1966 m cm^{-1} ; ^1H NMR (CDCl_3): 7.66 (m, 6H), 7.46 (m, 18H), 7.20 (m, 9H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 10.3 (s); MS (FAB): m/z 1378 (M^+).

*Thermolysis of $[\text{Ru}_3(\text{CO})_{10}(\text{PhPTh}_2)_2]$ **1***

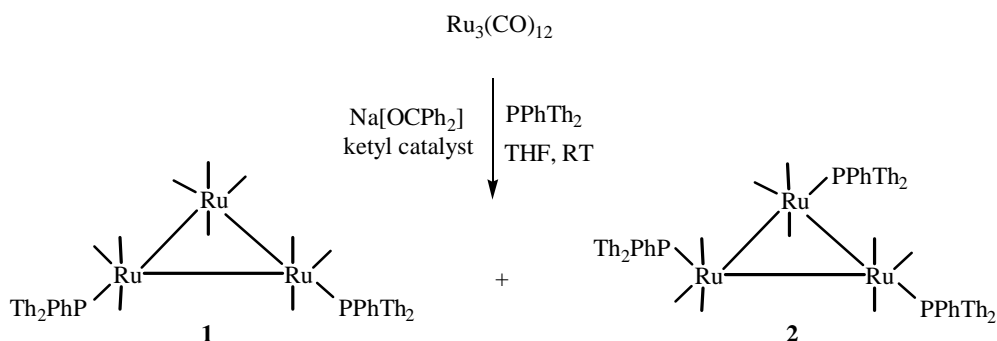
$[\text{Ru}_3(\text{CO})_{10}(\text{PhPTh}_2)_2]$ **1** (100 mg, 0.088 mmol) was heated in boiling benzene (20 mL) for 1 h during which time the colour of the solution changed from red to orange. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3, v/v) developed only one band which gave $[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-PhThP}(\text{C}_4\text{H}_2\text{S})\}(\text{PhPTh}_2)]$ **3** (66 mg, 69%) as orange crystals after recrystallization from hexane/ CH_2Cl_2 at 4°C. Spectral data for **3**: Anal. Calcd. for $\text{C}_{36}\text{H}_{22}\text{O}_8\text{P}_2\text{Ru}_3\text{S}_4$: C, 40.19; H, 2.07. Found: C, 40.56; H, 2.12%. IR (CO , CH_2Cl_2): 2070 s, 2028 s, 2013 s, 1197 m, 1961 m cm^{-1} ; ^1H NMR (CDCl_3): aromatic region (both

isomers): 7.94-6.26 (m); hydride region: major isomer: 17.05 (dd, $J_{P-H} = 20.8, 10.4$ Hz), minor isomer: 17.16 (dd, $J_{P-H} = 20.8, 10.4$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): major isomer: 18.6 (s), 17.5 (s); minor isomer: 32.7 (s), 23.8 (s); MS (FAB): m/z 1075 (M^+).

Results and discussion

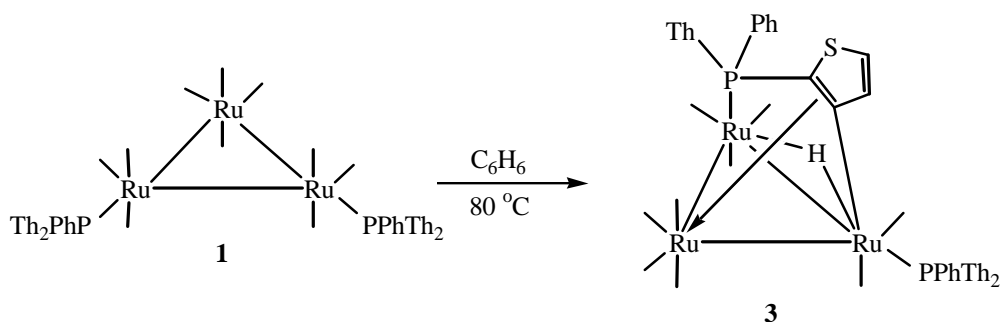
The reaction of $\text{Ru}_3(\text{CO})_{12}$ with PhPTh_2 in presence of catalytic amount of sodiumbenzophenone ketyl catalyst affords $[\text{Ru}_3(\text{CO})_{10}(\text{PhPTh}_2)_2]$ **1** and $[\text{Ru}_3(\text{CO})_9(\text{PhPTh}_2)_3]$ **2** in 45 and 10% yields, respectively (Scheme 1). Both compounds have been characterized by elemental analysis, IR, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and mass spectral data.

The carbonyl stretching region of the infrared spectra of both clusters are very similar to those of similar bis- and tris(phosphine) substituted triruthenium clusters found in literature.^{11,18} The ^1H NMR spectrum of both clusters display only aromatic resonances and the absence of hydride signals indicating that *ortho*-metallation had not taken place. The FAB mass spectrum of both clusters exhibits parent molecular ion (m/z 1131 for **1** and m/z 1378 for **2**) and ions due to sequential loss of all carbonyl ligands which is in accord with the proposed structures. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1** and **2** show only a singlet at 10.5 (s) and 10.3, respectively, the later indicating that cluster **1** exists in a single isomeric form in solution, i.e., in the *trans-trans* form with respect to Ru–Ru vector as shown in Scheme 1.

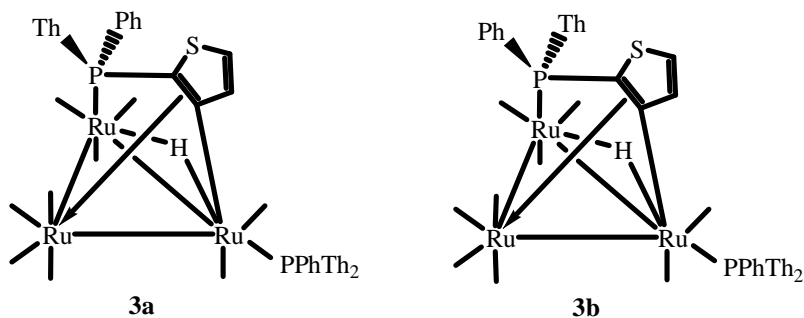


Scheme 1

As cluster **1** was obtained in good yield, we heated it in boiling benzene in order to get carbon-hydrogen and/or carbon-phosphorus bond cleavage of the coordinated PhPTh_2 ligand at elevated temperature. Indeed carbon-hydrogen bond cleavage has been observed at 80°C which results in the formation of $[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-PhThP}(\text{C}_4\text{H}_2\text{S})\}(\text{PhPTh}_2)]$ **3** in 69% yield (Scheme 2).



The pattern of the infrared spectrum in the carbonyl stretching region of **3** is very similar to that of its diphenyl(2-thienyl) analog $[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-Ph}_2\text{P}(\text{C}_4\text{H}_2\text{S})\}(\text{Ph}_2\text{PTh})]$ ¹¹ reported by Deeming *et al.* indicating that they have similar distribution of carbonyl ligands while the FAB mass spectrum of **3** exhibits a parent molecular ion at m/z 1075 together with ions due to successive loss of eight carbonyl ligands which are consistent with the proposed structure. The $^{31}\text{P}\{^1\text{H}\}$ NMR displays four singlets indicating the cluster **3** exists in two isomeric forms in solution (Chart 1). The intensity of these peaks suggests that two isomers are present in solution in 4:3 ratio. The aromatic region of the ^1H NMR spectrum is not informative which shows a series of multiplets between 7.94-6.26 for both isomers but the hydride region displays two clean doublet of doublets at 17.05 ($J_{\text{P-H}} = 20.8, 10.4$ Hz; major isomer) and 17.16 ($J_{\text{P-H}} = 20.8, 10.4$ Hz; minor isomer), shown in Figure 1.



There are several ways by which cluster **3** can adopt these two isomeric forms. But since the $J_{\text{P-H}}$ coupling constants are identical for both isomers, they are most likely formed by flipping of the phenyl and thienyl groups on the metalated phosphine ligands (Chart 1) as also observed for its osmium analog $[\text{Os}_3(\text{CO})_8\{\mu_3\text{-PhThP}(\text{C}_4\text{H}_2\text{S})\}(\text{PhPTh}_2)]$.¹⁵

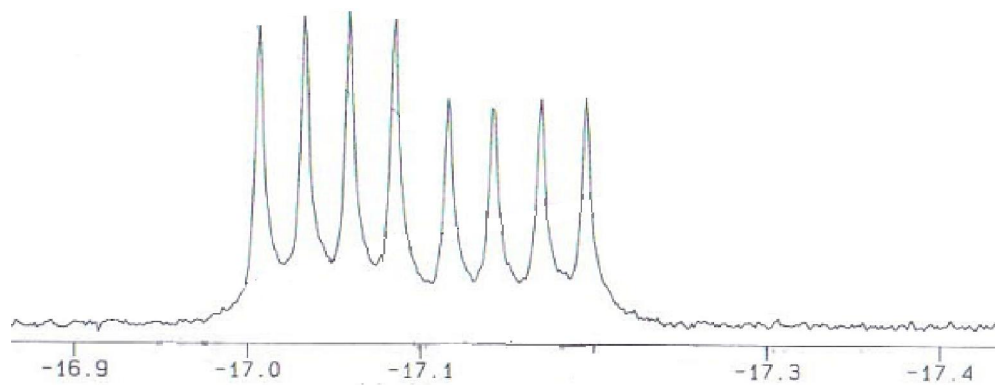


Fig. 1

Conclusion

The reaction between $\text{Ru}_3(\text{CO})_{12}$ and PhPTh_2 in presence of ketyl catalyst afforded bis- and tris(phosphine) substituted clusters **1** and **2**. Carbon-hydrogen bond cleavage was observed on heating **1** in boiling benzene resulted in the formation of the *ortho*-metalated cluster **3**. The overall reactivity of PhPTh_2 with $\text{Ru}_3(\text{CO})_{12}$ closely resembles that observed for $\text{Os}_3(\text{CO})_{12}$.¹⁵

Acknowledgement

We are grateful to Dr. Ebbe Nordlander, Center for Chemistry and Chemical Engineering, Lund University, Lund, Sweden for a generous gift of phenyldi(2-thienyl)phosphine. We also thank the University Grants Commission of Bangladesh for financial support.

References

1. R. J. Angelici, in R. B. King (Ed.), “*Encyclopedia of Inorganic Chemistry*”, Wiley, New York, 1994, Vol. 3, pp. 1433-1443.
2. H. Topsøe, B. S. Claussen and F. E. Massoth, in J. R. Anderson and M. Boudart (Eds.), “*Catalysis: Science and Technology*” Springer-Verlag, New York, 1996, Vol. 11.
3. R. J. Angelici, *Coord. Chem. Rev.*, 1990, **105**, 61.
4. R. J. Angelici, *Organometallics*, 2001, **20**, 1259
5. M. Brorson, J. D. King, K. Kiriakidou, F. Prestopino and E. Nordlander, in P. Braunstein, L. A. Oro and P. R. Raithby, “*Metal Clusters in Chemistry*” Wiley-VCH, Weinheim, 1999, Vol. 2, pp. 741-781.
6. R. J. Angelici, *Coord. Chem. Rev.*, 2000, **63**, 206-207

7. A. J. Deeming, M. K. Shinmar, A. J. Arce and Y. D. Sanctis, *J. Chem. Soc., Dalton Trans.*, 1999, 1153.
8. M. N. Uddin, M. A. Mottalib, N. Begum, S. Ghosh, A. K. Raha, D. T. Haworth, S. V. Lindeman, T. A. Siddiquee, D. W. Bennett, G. Hogarth, E. Nordlander and S. E. Kabir, *Organometallics*, 2009, **28**, 1514.
9. S. Ghosh, A. K. Das, N. Begum, D. T. Haworth, S. V. Lindeman, J. F. Gardinier, T. A. Siddiquee, D. W. Bennett, E. Nordlander, G. Hogarth and S. E. Kabir, *Inorg. Chim. Acta*, 2009, **362**, 5175.
10. U. Bodensieck, H. Varenkamp, G. Rheinwald and H. Stoeckli-Evans, *J. Organomet. Chem.*, 1995, **488**, 85.
11. A. J. Deeming, S. N. Jaysuriya, A. J. Arce and Y. D. Sanctis, *Organometallics*, 1996, **15**, 786.
12. M. N. Uddin, N. Begum, M. R. Hassan, G. Hogarth, S. E. Kabir, M. A. Miah, E. Nordlander and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 2008, 6219.
13. N. K. K. Kazemifar, M. J. Stchedroff, M. A. Mottalib, S. Selva, M. Monari and E. Nordlander, *Eur. J. Inorg. Chem.*, 2006, 2058.
14. M. A. Mottalib, S. E. Kabir, D. A. Tocher, A. J. Deeming and E. Nordlander, *J. Organomet. Chem.*, 2007, **692**, 5007.
15. S. Ghosh, G. Hogarth, D. A. Tocher, E. Nordlander and S. E. Kabir, *Inorg. Chim. Acta*, 2010, **363**, 1611.
16. S. P. Tunik, I. G. Koshevoy, A. J. Poë, D. H. Farrar, E. Nordlander, M. Haukka and P. A. Pakkanen, *J. Chem. Soc., Dalton Trans.*, 2003, 2457.
17. J. D. King, M. Monari and E. Nordlander, *J. Organomet. Chem.*, 1999, **573**, 272.
18. N. Begum, M. A. Rahman, M. R. Hassan, D. A. Tocher, E. Nordlander, G. Hogarth and S. E. Kabir, *J. Organomet. Chem.*, 2008, **693**, 1645.

(Received : 12 July, 2011; Accepted : 30 November, 2011)

Table of contents entry**CARBON-HYDROGEN BOND
ACTIVATION OF PHENYLDI(2-
THIENYL)PHOSPHINE AT A
TRIRUTHENIUM CLUSTER
CENTER**SHAHED RANA, SHISHIR GHOSH
AND SHARIFF E. KABIR*Reactivity of phenyldi(2-thienyl)phosphine with $\text{Ru}_3(\text{CO})_{12}$
has been investigated.