Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Reaction of ruthenium phenyl acetylide with iron-chalcogen clusters and iron pentacarbonyl

Pradeep Mathur^{a,b,*}, Abhinav Raghuvanshi^a, Radhe Shyam Ji^a, Shaikh M. Mobin^{b,c}

^a Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

^b School of Sciences, Indian Institute of Technology Indore, Khandwa Road, Indore 452017, India

^c Sophisticated Instrumentation Centre, Indian Institute of Technology Indore, Khandwa Road, Indore 452017, India

ARTICLE INFO

Article history: Received 5 November 2012 Received in revised form 1 February 2013 Accepted 4 February 2013

Keywords: Ruthenium acetylide Photolysis Adduct Mixed metal cluster

ABSTRACT

Photolysis of a THF solution containing ruthenium acetylide $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$ with $[Fe_3(CO)_9(\mu_3-Se)_2]$ cluster affords an adduct $[\{\mu-SeC(CpRu(PPh_3)(CO))=C(Ph)Se\}(CO)_6Fe_2]$ (1), while under similar reaction condition with $[Fe_3(CO)_9(\mu_3-Te)_2]$ cluster a Ru-inserted product $[(\eta^5-C_5H_5)(PPh_3)(\eta^1-C=CPh)RuFe_2(\mu_3-Te)_2(CO)_6]$ (2) was obtained. Under thermal condition $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$ react with $Fe(CO)_5$ to give an acetylide stabilised Fe_2Ru mixed metal cluster $[(\eta^5-C_5H_5)RuFe_2(CO)_7(\eta^2:\eta^2:\eta^1-C=CPh)]$, (3).

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Chemistry of metal acetylide complexes continues to attract attention for the construction of organometallic polymers [1-7]and as components in non-linear optical materials [8-10]. Mononuclear acetylide complexes are versatile building blocks in cluster growth reactions and a number of polycarbon ligand-containing metal clusters have been prepared from mononuclear metal acetylides [11–16]. As part of our studies on chalcogen-bridged clusters, we have observed that when chalcogen-bridged metal carbonyl compounds are used as precursors to react with metal acetylide molecules, an equally rich and diverse set of acetylideincorporated mixed-metal clusters form, where the nature of metal acetylide additions and acetylide coupling are strongly dependent on the nature of chalcogen used, the metal atom present and also the reaction conditions [17-20]. Previously, we have reported the reactivity of mononuclear acetylide complexes $[(\eta^5 C_5H_5$)M(CO)₃(η^1 -C=CPh)] (M = Mo or W) with [Fe₃(CO)₉(μ_3 -E)₂] (E = S, Se, Te), where formation of a number of different Fe₃M₂E₂ or Fe₄M₂E₂ type clusters was observed, having head-to-head, head-totail and tail-to-tail coupling of two multi-coordinated acetylide units, and also the ones which contain two acetylide groups which

are bridged head-to-head by a $[Fe(CO)_2]$ unit [17-19]. Further, in some clusters the acetylide units remained uncoupled [20].

More variations are also expected by using different types of metal acetylides with chalcogen-bridged metal carbonyl compounds and different metal carbonyls. In this paper, we report on our investigation on reactions of a non-carbonyl metal acetylide $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C\equiv CPh)]$ with $[Fe_3(CO)_9(\mu_3-E)_2]$ (E=Se or Te)] and with iron pentacarbonyl. Motivation for this study was to obtain a new strategy for the formation of mixed metal and mixed metal-chalcogen clusters.

2. Results and discussion

2.1. Reaction of $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C\equiv CPh)]$ with $[Fe_3(CO)_9(\mu_3-E)_2]$

When a THF solution containing $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$ and $[Fe_3(CO)_9(\mu_3-Se)_2]$ was photolysed under continuous bubbling of nitrogen at 0 °C for 30 min, a formal adduct, of $[(\eta^5-C_5H_5)Ru(PPh_3)(CO)(C=CPh)]$ and $[Fe_2(CO)_6(\mu-Se_2)]$, $[\{\mu-SeC(C-pRu(PPh_3)(CO))=C(Ph)Se\}(CO)_6Fe_2]$ (1) was obtained, along with the known compounds $[Fe_3(CO)_8PPh_3(\mu_3-Se)_2]$, $[Fe_2(CO)_5PPh_3(\mu-Se)_2]$ and $SePPh_3$ (Scheme 1).

In contrast, when a THF solution containing $[(\eta^5-C_5H_5)$ Ru(PPh₃)₂($\eta^1-C\equiv$ CPh)] and $[Fe_3(CO)_9(\mu_3-Te)_2]$ was photolysed at 0 °C for 30 min, under nitrogen atmosphere, formation of a new



^{*} Corresponding author. School of Sciences, Indian Institute of Technology Indore, Khandwa Road, Indore 452017, India. Tel.: +91 7312368282.

E-mail addresses: mathur@iitb.ac.in, mathur@chem.iitb.ac.in (P. Mathur).

⁰⁰²²⁻³²⁸X/\$ - see front matter \odot 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2013.02.001



Scheme 1. Photolysis of $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C\equiv CPh)]$ with $[Fe_3(CO)_9(\mu_3-E)_2]$.

ruthenium inserted mixed metal cluster $[(\eta^5-C_5H_5)(PPh_3)(\eta^1-C \equiv CPh) \text{ RuFe}_2(\mu_3-Te)_2(CO)_6]$, (2) was observed along with $[Fe_3(CO)_8PPh_3(\mu_3-Te)_2]$ and $[Fe_2(CO)_5PPh_3(\mu-Te_2)]$ (Scheme 1).

Compounds **1** and **2** were found to be stable in solid state under inert atmosphere but gradually decompose in air. Suitable single crystals of **1** and **2** were grown from hexane/dichloromethane solvent mixture and their structures were established crystallographically. The IR spectra of **1** and **2** display a carbonyl stretching pattern typically observed in the spectra of compounds containing the $[Fe_2(CO)_6]$ group. ¹H NMR spectra of **1** and **2** confirm the presence of phenyl and cyclopentadienyl groups.

The yields of **1** and **2** are rather low surprisingly, because even under mild conditions and even in presence of stabilising bridging chalcogen ligands we get a large amount of triphenylphosphine substituted clusters [Fe₃(CO)₈PPh₃(µ₃-E)₂], [Fe₂(CO)₅PPh₃(µ₂-E₂)] (E = Se and Te) and [SePPh₃], which indicates some amount of cluster degradation. It is envisaged that in both the reactions, under photolytic condition, a reactive coordinatively unsaturated species, $[(\eta^5-C_5H_5)Ru(PPh_3)(\eta^1-C=CPh)]$ is initially formed, which in the case of the reaction with [Fe₃(CO)₉(µ₃-Se)₂] adds a CO and then forms the adduct **1**, whereas in the case of reaction with [Fe₃(CO)₉(µ₃-Te)₂], adds directly to form the adduct **2**. We have not found the formation of complex type **2** with Se-cluster and formation of complex type **1** with Te-cluster. Also, isomerisation of **1** and **2** was not observed on heating.

The molecular structure of **1**, shown in Fig. 1, consists of a butterfly $[Fe_2(CO)_6Se_2]$ unit and $[CpRu{PPh_3(CO)}C=CPh]$ unit added across the open butterfly edge. Structure of **1** is similar to numerous adducts obtained from the reaction of terminal acetylenes with $[Fe_2(CO)_6(\mu-E_2)]$ complexes (E = S, Se and Te) [21–23]. However, this is the first example of a formal adduct formation with an internal acetylene. In compound **1**, one of the PPh₃ ligands on the ruthenium is substituted by a CO ligand, probably due to the steric interactions between the two PPh₃ ligands.

Overall, the structure of **1** is similar to $[\{\mu-SeC(H)=C(Ph) \in E\}(CO)_6Fe_2]$ (E = S [24], Se [25], Te [26]), $[\{\mu-SC(H)=C(Ph) = C(Ph)Te\}(CO)_6Fe_2]$ [25], $[\{\mu-TeC(H)=C(Ph)Te\}(CO)_6Fe_2]$ [21], $[\{\mu-SeC(H)=C(2-Th)Se\}(CO)_6Fe_2]$ [23], and $[\{\mu-SC(C=CCH_3)=C(H)Te\}-(CO)_6Fe_2]$ [24]. The C-C bond distance of 1.328(6) Å indicates the reduction of the acetylenic triple bond to an olefinic bond and is similar to corresponding bond distances of the coordinated acetylenic bond in [$\{\mu-SeC(H)=C(Ph)S\}(CO)_6Fe_2$] (1.293(13) Å) [24], [$\{\mu-SeC(H)=C(Ph)Se_2(CO)_6Fe_2$] (1.331(7) Å) [25], [$\{\mu-SeC(H)=C(Ph)Te\}(CO)_6Fe_2$]



Fig. 1. ORTEP diagram of compound 1 with 50% probability ellipsoids: Selected bond lengths (Å) and bond angles (deg): Fe(1)–Fe(2) = 2.5323(9), Ru(1)–C(15) = 1.843(5), Ru(1)–C(1) = 2.071(5), C(1)–C(2) = 1.328(6), C(2)–C(3) = 1.481(6), Se(1)–C(1) = 1.993(4), Se(2)–C(2) = 1.980(4), Fe(1)–Se(1) = 2.3897(8), Fe(1)–Se(2) = 2.3727(9), Fe(2)–Se(1) = 2.3793(9), Fe(2)–Se(2) = 2.3705(8) and O(1)–C(15)–Ru(1) = 173.5(5), C(1)–Se(1)–Fe(1) = 101.62(13), C(1)–Se(1)–Fe(2) = 105.38(14), C(2)–Se(2)–Fe(2) = 103.73(13), C(2)–Se(2)–Fe(1) = 98.99(14). Se(2)–Fe(1)–Se(1) = 79.81(3), Se(2)–Fe(2)–Se(1) = 80.07(3).



Fig. 2. ORTEP diagram of compound 2 with 50% probability ellipsoids: Selected bond lengths (Å and bond angles (deg): Fe(1)-Fe2) = 2.6136(19), Ru(1)-C(7) = 2.023(10), Ru(1)-Te(2) = 2.7424(10), Ru(1)-Te(1) = 2.7425(9), C(7)-C(8) = 1.215(12), Fe(1)-Te(1) = 2.5468(17), Fe(1)-Te(2) = 2.5505(16), Fe(2)-Te(2) = 2.5153(14), Fe(2)-Te(1) = 2.5724(15) and C(7)-C(8)-C(9) = 176.6(10), Te(2)-Ru(1)-Te(1) = 66.21(2), Te(1)-Fe(1)-Te(2) = 71.99(4), Te(2)-Te(1) = 72.14(4).

(1.31(1) Å) [26], [{ μ -TeC(H)=C(Ph)Te}(CO)_6Fe_2] (1.34(1) \text{ Å}) [21], $[\{\mu-SeC(H)=C(2-Th)Se\}(CO)_{6}Fe_{2}]$ (1.306(14) Å) [27], and $[\{\mu-SeC(H)=C(2-Th)Se\}(CO)_{6}Fe_{2}]$ $SC(C \equiv CCH_3) = C(H)Te - (CO)_6Fe_2 (1.31(1) Å) [28].$ The Fe-Fe bond distance of 2.5323(9) Å in 1 is shorter than the corresponding distance in $[{\mu-TeC(H)=C(Ph)Te}(CO)_6Fe_2]$ (2.571(4) Å) [21], but comparable with the 2.539(5) Å in $[\{\mu-SeC(H)=C(Ph)Te\}(CO)_6Fe_2]$ [26] and 2.513(9) Å in $[{\mu-SeC(H)=C(2-Th)Se}(CO)_6Fe_2]$ [23]. It is similar to the 2.501(3) Å in $[{\mu-SeC(H)=C(Ph)S}(CO)_6Fe_2]$ [24]. The Fe–Se bond lengths of 2.3897(8) Å and 2.3705(8) Å in 1 compare well with the average Fe–Se bond length of 2.382(2) Å in [$\{\mu$ -SeC(H)=C(2-Th)Se}(CO)₆Fe₂] [27] and, 2.3792(9) Å and 2.3901(9) in $[\{\mu-SeC(H)=C(Ph)Se\}(CO)_6Fe_2]$ [25]. The average Se-Fe-Se bond angle of 79.9° is similar to the average Se-Fe-Se bond angle of 81.3° and 81.4° in [{µ-SeC(H)=C(2-Th)Se}(CO)₆Fe₂] [23] and [{µ-SeC(H)= C(Ph)Se}(CO)₆Fe₂] [25] respectively, but is greater than the average Se-Fe-Se bond angle of 58° in the closed tetrahedron of $[(CO)_6Fe_2(\mu-Se_2)]$ [28]. This widening of bond angle is consistent with an opening of the Fe₂Se₂ butterfly core to accommodate the ruthenium-acetvlide molecule.

Formation of chalcogen bridged and acetylide-bearing mixed metal clusters has been reported previously by our group from the thermolytic reaction of [Fe₃(CO)₉(μ_3 -E)₂] clusters (E = Se, Te) and [(η^5 -C₅H₅)M(CO)₃(η^1 -C=CPh)] (M = Mo, W) [20]. However, crystal structure of only the selenium compound, [(η^5 -C₅H₅)MoFe₂(μ_3 -Se)₂(CO)₆(η^1 -C=CPh)] has been reported; where it consists of a [Fe₂MoSe₂] distorted square pyramidal core with the Mo atom at

the apical site. Compound **2** in contrast consists of an open Fe_2Te_2 butterfly with the Ru atom bridging the Te wing-tips (Fig. 2).

The structure of **2** is comparable with $[(CO)_6Fe_2(\mu-TeCH_2Te)]$ [29] and $[(\pi - C_8 H_{12})Pt(\mu_3 - Te)_2 Fe_2(CO)_6]$ [30]. Fe-Fe bond distance of 2.6136(19) Å is slightly longer than the corresponding distance in $[\{\mu - \text{TeC}(H) = C(Ph)\text{Te}\}(CO)_6\text{Fe}_2](2.571(4) \text{ Å})[21], [\{\mu - \text{SeC}(H) = C(Ph)\}$ Te}(CO)₆Fe₂] (2.539(5) Å) [26] and $[(CO)_6Fe_2 (\mu-TeCH_2Te)]$ (2.587(2) Å) [30] but is comparable to 2.6120(19) Å in $[(\pi-C_8H_{12})Pt(\mu_3-$ Te)₂Fe₂(CO)₆] [30]. The Fe–Te bond lengths 2.5468(17) Å and 2.5153(14) Å are slightly smaller than the 2.5889(15) Å and 2.5666(16) Å in [(π-C₈H₁₂)Pt(μ₃-Te)₂Fe₂(CO)₆] [30], and 2.551(2) Å and 2.544 (2) Å in [(CO)₆Fe₂ (µ-TeCH₂Te)] [29]. The average Te-Fe-Te bond angle of 72.1° is less than the average Te–Fe–Te bond angle of 79.1° and 75.4° in $[(\pi-C_8H_{12})Pt(\mu_3-Te)_2Fe_2(CO)_6]$ [30] and [(CO)₆Fe₂ (µ-TeCH₂Te)] [29], respectively. The Cp and the PPh₃ ligands expectedly cause as the constriction of the butterfly as seen in the Te-Ru-Te bridging angle of 66.21° which is much smaller than the Te-Pt-Te bond angle of 79.08(3)° in $[(\pi-C_8H_{12})Pt(\mu_3 Te_{2}Fe_{2}(CO)_{6}$ [30] and $Te-CH_{2}$ -Te bond angle 92.1(4)° in $[(CO)_6Fe_2(\mu\text{-TeCH}_2Te)]$ [29].

2.2. Reaction of $[(\eta^5 - C_5H_5)Ru(PPh_3)_2(\eta^1 - C \equiv CPh)]$ with iron pentacarbonyl

In contrast to the reactions of $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C\equiv CPh)]$ with $[Fe_3(CO)_9(\mu_3-E)_2]$, even after extended photolysis of a THF



Scheme 2. Thermolysis of $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C\equiv CPh)]$ with Fe(CO)₅.



Fig. 3. ORTEP diagram of compound 3 with 50% probability ellipsoids: Selected bond lengths (Å) and bond angles (deg): C(9)-C(10) = 1.462(3), C(8)-C(9) = 1.331(3), Ru(1)-C(8) = 2.1396(19), Ru(1)-C(9) = 2.133(2), Ru(1)-C(7) = 1.880(2), Fe(1)-C(7) = 2.369(2), Fe(1)-C(8) = 2.038(2), Fe(1)-C(9) = 2.083(2), Fe(2)-C(8) = 1.815(2), Fe(1)-Fe(2) = 2.6343(4), Ru(1)-Fe(1) = 2.6117(3), Ru(1)-Fe(2) = 2.6843(3) and Fe(1)-Ru(1)-Fe(2) = 59.639(9), Ru(1)-Fe(1)-Fe(2) = 61.550(9), Fe(1)-Fe(2)-Ru(1) = 58.811(9), O(7)-C(7)-Ru(1) = 159.71(18), O(7)-C(7)-Fe(1) = 125.41(16).

solution containing the ruthenium acetylide and $[Fe(CO)_5]$ no new product formation was observed.

When a toluene solution containing $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$ and $[Fe(CO)_5]$ was heated at 100 °C for 7 h, under a nitrogen atmosphere, a new green coloured mixed metal cluster, $[(\eta^5-C_5H_5)RuFe_2(CO)_7(\eta^2:\eta^2:\eta^1-C=CPh)]$, **3** was obtained along with $[Fe(CO)_4PPh_3]$ (Scheme 2). Compound **3** was found to be stable in solid state under inert atmosphere but it gradually decomposes in air. The infrared spectrum of **3**, shows CO stretching pattern in the range 1960–2063 cm⁻¹, indicating the presence of semibridging and terminal carbonyls. Suitable single crystals of **3** were grown from hexane/dichloromethane solvent mixture and its structure was established crystallographically.

The molecular structure of **3**, shown in Fig. 3, consists of Fe₂Ru triangular core, capped by the acetylide moiety. While both Fe atoms bear three terminal CO groups, a CO group bonded to Ru shows a semi-bridging character towards Fe(1), as Ru(1)-C(7)-O(7) bond angle is $159.71(18)^{\circ}$. Of the three metal-metal bonds, CO bridged Ru(1)-Fe(1) bond is the shortest, Fe(1)-Fe(2) = 2.6343(4) Å, Ru(1)-Fe(1) = 2.6117(3) Å and Ru(1)-Fe(2) = 2.6843(3) Å. Important feature of compound **3** is the change in bonding mode of acetylide towards ruthenium. Ruthenium, which was initially bonded to acetylide in η^1 -fashion in reactant, is bonded to acetylide in $\eta^2\mbox{-}fashion$ in the product (Ru(1)-C(8) = 2.1396(19), Ru(1)-C(9) = 2.133(2) Å). This type of interchange has been established for binuclear [31] and polynuclear [32-37] complexes containing μ -alkynyl ligands. Fe(1) is also bonded to acetylide in η^2 -fashion, (Fe(1)–C(8) = 2.038(2), Fe(1)-C(9) = 2.083(2), Fe(2)-C(8) = 1.815(2) Å whereas Fe(2)acetylide bond is η^{I} .

The most significant part of the reaction is that the main product **3** does not contain any phosphine unit, which indicates, under the harsher reaction condition, not one but both phosphines dissociate from the $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$, probably in a stepwise manner. This is a very interesting observation that $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$ can be a very good source of giving either

 $[(\eta^5-C_5H_5)Ru(PPh_3)(C \equiv CPh)]$ under photolytic condition or $[(\eta^5-C_5H_5)Ru(\eta^1-C \equiv CPh)]$ which can be obtained under thermolytic conditions. Both of these highly reactive species can be very good synthons for cluster growth reactions.

The acetylide unit acts as a five electron donor to the cluster core. Compound **3** is an electron precise system having 48 cluster valence electrons, but the formal electron counts for Ru1, Fe1 and Fe2 are 19, 18 and 17 and surprisingly, it is the bond between the 19-electron Ru1 and the 18-electron Fe1 which is spanned by a semibridging carbonyl.

3. Conclusion

In conclusion, we have investigated the reactions of noncarbonyl containing ruthenium acetylide $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$ with $[Fe_3(CO)_9(\mu_3-E)_2]$ (E = Se or Te)] clusters and with iron pentacarbonyl. The first example of an adduct of internal acetylene was obtained in the reaction with $[Fe_3(CO)_9(\mu_3-Se_2)]$; whereas, with $[Fe_3(CO)_9(\mu_3-Te_2)]$, a formal Ru insertion to the Fe_2Te_2 butterfly and a formation of Fe_2Te_2Ru cluster was observed. In the reaction of iron-pentacarbonyl, an acetylide stabilised Fe_2Ru mixed-metal cluster was obtained. It was also observed that, under photolytic conditions $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$ loses one phosphine to give $[(\eta^5-C_5H_5)Ru(PPh_3)(\eta^1-C=CPh)]$, whereas, under thermal conditions, it loses both phosphines, probably in a stepwise manner, to give $[(\eta^5-C_5H_5)Ru(\eta^1-C=CPh)]$, which can be an important reactive unit in cluster growth reactions.

4. Experimental section

4.1. General procedures

All reactions and manipulations were performed using standard Schlenk line techniques under an inert atmosphere of pre-purified nitrogen or argon. Solvents were purified, dried and distilled under argon or nitrogen atmosphere prior to use. Infrared spectra were P. Mathur et al. / Journal of Organometallic Chemistry 731 (2013) 55-60

Table 1	
Crystal data and	structure refinement for compound

1 to 3

Compound	1	2	3
Empirical formula	C ₃₈ H ₂₅ Fe ₂ O ₇ PRuSe ₂	C ₃₇ H ₂₅ Fe ₂ O ₆ PRuTe ₂	C ₂₀ H ₁₀ Fe ₂ O ₇ Ru
Formula wt.	995.24	1064.51	575.05
Crystal system	Triclinic	Triclinic	Monoclinic
Spacegroup	P-1	P-1	<i>P</i> 2 ₁ /n
a, Å	10.8550(10)	8.5830(8)	15.0337(3)
b, Å	11.2875(11)	11.1868(12)	8.6218(2)
<i>c</i> , Å	17.6763(7)	20.4292(19)	15.7257(4)
α, deg	82.480(5)	96.924(8)	90
β, deg	82.019(5)	101.557(8)	104.995 (2)
γ, deg	61.455(10)	104.830(9)	90
Volume, Å ³	1878.9(3)	1826.9(3)	1968.92(8)
Ζ	2	2	4
$D_{\text{calcd}}, \text{Mg/m}^3$	1.759	1.935	1.940
Abs coeff, mm ⁻¹	3.186	2.845	2.252
F(000)	976	1020	1128
Crystal size, mm	$0.33 \times 0.26 \times 0.21$	$0.38\times0.33\times0.28$	$0.33 \times 0.26 \times 0.21$
θ range, deg	3.31-25.00	2.95-25.00	3.21-25.00
Index ranges	$-10 \le h \le 12$, $-10 \le k \le 13$,	$-10 \le h \le 7, -13 \le k \le 13,$	$-17 \leq h \leq 16$, $-10 \leq k \leq 10$,
	$-21 \le l \le 21$	$-24 \le l \le 24$	$-18 \leq l \leq 18$
Reflections collected/unique	13670/6602 [R(int) = 0.0371]	$14299/6417 \ [R(int) = 0.0786]$	15282/3461 [R(int) = 0.0258]
Completeness to $\theta = 25$	99.8%	99.8%	99.8%
Data/restraints/parameters	6602/0/460	6417/0/442	3461/0/271
Goodness-of-fit on F ²	1.009	1.017	1.054
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0379$, $wR_2 = 0.0802$	$R_1 = 0.0638, wR_2 = 0.1438$	$R_1 = 0.0199, wR_2 = 0.0470$
R indices (all data)	$R_1 = 0.0593$, $wR_2 = 0.0896$	$R_1 = 0.0897$, $wR_2 = 0.1694$	$R_1 = 0.0234, wR_2 = 0.0485$
Largest diff. peak and hole	0.871 and –0.472 e A ⁻³	1.938 and -1.420 e A ⁻³	0.329 and -0.405 e A ⁻³

recorded on Perkin Elmer FTIR spectrometer. NMR spectra were recorded on Bruker AVANCE III/400 spectrometer with TMS as internal standard. Iron pentacarbonyl, and phenyl acetylene were purchased from Fluka, and Aldrich, respectively, and were used without further purification. $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C=CPh)]$ [38] Fe₃(CO)₉(μ_3 -Se)₂ [39] and [Fe₃(CO)₉(μ_3 -Te)₂] [40] were prepared as described previously. Photochemical reactions were carried out in a water cooled double-walled quartz vessel having a 125 W mercury lamp manufactured by SAIC, India. TLC plates were purchased from Merck (20 × 20 cm, silica gel 60 F254).

4.2. Synthesis of $[{\mu-SeC(CpRu(PPh_3)(CO))=C(Ph)Se}(CO)_6Fe_2]$ (1)

To a solution of $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C\equiv CPh)]$ (79 mg, 0.1 mmol), in THF, $[Fe_3(CO)_9(\mu_3-Se)_2]$ (116 mg, 0.2 mmol) was added and the solution was photolysed at 0 °C for 30 min under a nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue was subjected to a chromatographic workup on silica gel TLC plates. Elution with dichloromethane/hexane solvent mixture yielded 14 mg (14%) of compound **1** along with $[Fe_3(CO)_8PPh_3(\mu-Se)_2]$, $[Fe_2(CO)_5PPh_3(\mu-Se)_2]$ and SePPh_3. IR (ν_{CO} in hexane): 2073 cm⁻¹, 2035 cm⁻¹, 2027 cm⁻¹, 1993 cm⁻¹

IR (ν_{CO} in hexane): 2073 cm⁻¹, 2035 cm⁻¹, 2027 cm⁻¹, 1993 cm⁻¹ indicate the presence of terminal carbonyls. ¹H NMR (δ , CDCl₃): 5.04 ppm (5H, Cp protons), 7.17–7.42 ppm (20H, Ph protons). MS (m/z, ES+): 995.5 (M⁺). Anal. Calc. for C₃₈H₂₅Fe₂O₇PRuSe₂: C, 45.86; H, 2.53. Found: C, 45.49; H, 2.79%.

4.3. Synthesis of $[(\eta^5-C_5H_5)(PPh_3)(\eta^1-C\equiv CPh)RuFe_2(\mu_3-Te)_2(CO)_6]$ (2)

To a solution of $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C\equiv CPh)]$ (79 mg, 0.1 mmol), in THF, [Fe₃(CO)₉(μ_3 -Te)₂] (136 mg, 0.2 mmol) was added and the solution was photolysed at 0 °C for 30 min under a nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue was subjected to a chromatographic workup on silica gel TLC plates by using dichloromethane/hexane solvent mixtures as eluent, which afforded 9 mg (8%) of compound **2** along with [Fe₃(CO)₈PPh₃(μ -Te)₂] and [Fe₂(CO)₅PPh₃(μ -Te₂)].

IR (ν_{CO} in hexane): 2072 cm⁻¹, 2033 cm⁻¹, 1992 cm⁻¹ indicate the presence of terminal carbonyls. ¹H NMR (δ , CDCl₃): 5.1 ppm (5H, Cp protons), 7.11–7.52 ppm (20H, Ph protons). MS (m/z, ES+): 1064.6 (M⁺). Anal. Calc. for C₃₇H₂₅Fe₂O₆PRuTe₂: C, 41.75, H, 2.37. Found: C, 41.32, H 2.52%.

4.4. Synthesis of $[(\eta^5 - C_5 H_5) RuFe_2(CO)_7(\eta^2:\eta^2:\eta^1 - C = CPh)]$ (3)

To a 10 ml toluene solution of $[(\eta^5-C_5H_5)Ru(PPh_3)_2(\eta^1-C\equiv CPh)]$ (79 mg, 0.1 mmol), [Fe(CO)₅] (0.2 ml, 1.46 mmol) was added and the mixture was heated at 100 °C for 7 h under nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue was subjected to chromatographic workup on silica gel TLC plates by using dichloromethane/hexane solvent mixtures as eluent, which afforded 12 mg (21%) of green coloured compound **3** along with [Fe(CO)₄PPh₃].

IR (ν_{CO} in hexane): 2063 cm⁻¹, 2043 cm⁻¹, 2021 cm⁻¹, 1995 cm⁻¹, 1960 cm⁻¹ indicate the presence of terminal and semibridging carbonyls. ¹H NMR (δ , CDCl₃): 5.22 ppm (5H, Cp protons), 7.34–7.71 ppm (5H, Ph protons), MS (m/z, ES+): 575.1 (M⁺). Anal. Calc. for C₂₀H₁₀Fe₂O₇Ru: C, 41.77, H, 1.75. Found: C, 41.47, H, 1.88%.

4.5. Crystal data of compound 1 to 3

Relevant crystallographic data and structure refinement details are listed in Table 1. Suitable X-ray quality crystals of compounds **1**, **2** and **3** were grown by slow evaporation of n-hexane and dichloromethane. An Oxford Diffraction X calibur-S/Supernova diffractometer were used for the cell determination and intensity data collection. Monochromatic Mo K α radiation (0.71359 Å) was used for the measurements. Absorption corrections using multi ψ scans were applied. The structures were solved by direct methods (SHELXS) and refined by full matrix least squares against F_0^2 using SHELXL-97 software [41]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. The crystal and refinement data are summarized in Table 1.

Acknowledgements

P.M. is grateful to the Department of Science and Technology, Government of India for support. A.R. and R.S.J. are grateful to CSIR, Government of India for research fellowships.

Appendix A. Supplementary material

CCDC 898446, 898444, and 898445 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

- [1] K.A. Williams, A.J. Boydston, C.W. Bielawski, Chem. Soc. Rev. 36 (2007) 729-744.
- [2] K. Onitsuka, A. Shimizu, S. Takahashi, Chem. Commun. (2003) 280–281.
 [3] M.S. Khan, A.K. Kakkar, S.L. Ingham, P.R. Raithby, J. Lewis, B. Spencer,
- F. Wittmann, R.H. Friend, J. Organomet. Chem. 472 (1994) 247–255. [4] C.W. Faulkner, S.L. Ingham, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby,
- J. Organomet. Chem. 482 (1994) 139-145.
- [5] A. Abe, N. Kimura, S. Tabata, Macromolecules 24 (1991) 6238–6243.
 [6] H.B. Fyfe, M. Mlekuz, D. Zergarian, N.J. Taylor, T.B. Marder, Chem. Commun.
- (1991) 188–190.
- [7] G. Gia, N.C. Payne, J.J. Vittal, R.J. Puddephatt, Organometallics 12 (1993) 4771–4778.
- [8] C.E. Powell, M.G. Humphrey, Coord. Chem. Rev. 248 (2004) 725-756.
- [9] S.R. Marder, J.E. Sohn, G.D. Stucky, ACS Symp. Ser. 605 (1991) 455 (and references therein).
- [10] P.N. Prasad, D.J. Williams, Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.
- [11] P. Blenkiron, G.D. Enright, A.J. Carty, Chem. Commun. (1997) 483-484.
- [12] Y. Chi, A.J. Carty, P. Blenkiron, E. Delgado, G.D. Enright, W. Wang, S.-M. Peng, G.-H. Lee, Organometallics 15 (1996) 5269–5271.
- [13] C.-H. Wu, Y. Chi, S.-H. Peng, G.-H. Lee, J. Chem. Soc. Dalton Trans. (1990) 3025-3031.
- [14] E. Delgado, Y. Chi, W. Wang, G. Hogarth, P.J. Low, G.D. Enright, S.-M. Peng, G.-H. Lee, A.J. Carty, Organometallics 17 (1998) 2936–2938.
- [15] A.J. Carty, G. Hogarth, G. Enright, G. Frapper, Chem. Commun. (1997) 1883-1884.

- [16] C.W. Pin, Y. Chi, C. Chung, A.J. Carty, S.-M. Peng, G.-H. Lee, Organometallics 17 (1998) 4146–4154.
- [17] P. Mathur, M.O. Ahmed, A.K. Dash, M.G. Walawalkar, J. Chem. Soc. Dalton Trans. (1999) 1795–1798.
- [18] P. Mathur, M.O. Ahmed, A.K. Dash, M.G. Walawalkar, V.G. Puranik, J. Chem. Soc. Dalton Trans. (2000) 2916-2922.
- [19] P. Mathur, M.O. Ahmed, J.H. Kaldis, M.J. McGlinchey, J. Chem. Soc. Dalton Trans. (2002) 619-629.
- [20] P. Mathur, A.K. Bhunia, A. Kumar, S. Charrerjee, S.M. Mobin, Organometallics 21 (2002) 2215–2218.
- [21] Th. Fässler, D. Buchhloz, G. Huttner, L. Zsolnai, J. Organomet. Chem. 369 (1989) 297–308.
- [22] P. Mathur, A.K. Dash, J. Cluster Sci. 9 (1998) 131-143.
- [23] P. Mathur, A.K. Dash, M.M. Hossain, C.V.V. Satyanarayana, A.L. Rheingold, G.P.A. Yap, L.M. Liable-Sands, J. Organomet. Chem. 543 (1997) 135–143.
- [24] P. Mathur, A.K. Dash, M.M. Hossain, S.B. Umbarkar, C.V.V. Satyanarayana, Y.-S. Chen, E.M. Holt, S.N. Rao, M. Soriano, Organometallics 15 (1996) 1356-1361.
- [25] P. Mathur, M.M. Hossain, Organometallics 12 (1993) 2398-2400.
- [26] P. Mathur, M.M. Hossain, S.B. Umbarkar, C.V.V. Satyanarayana, S.S. Tavale, V.G. Puranik, Organometallics 14 (1995) 959–963.
- [27] P. Mathur, M.M. Hossain, S.N. Datta, R.-K. Kondru, M.M. Bhadbhade, Organometallics 13 (1994) 2532–2535.
- [28] C.F. Campana, F. Lo, L.F. Dahl, Inorg. Chem. 18 (1979) 3060-3064.
- [29] P. Mathur, V.D. Reddy, R. Bohra, J. Organomet. Chem. 401 (1991) 339–346.
 [30] A.A. Pasynskii, N.I. Semenova, Yu.V. Torubaev, P.V. Belousov, K.A. Lyssenko,
- [30] A.A. Pasynskii, N.I. Semenova, Yu.V. Torubaev, P.V. Belousov, K.A. Lyssenko Zh.V. Dobrokhotova, Russ. Chem. Bull. Int. Ed. 50 (2001) 2215–2220.
- [31] M. Akita, M. Terada, S. Oyama, Y. Morooka, Organometallics 9 (1990) 816– 825.
- [32] Y. Chi, B.-J. Liu, G.-H. Lee, S.-M. Peng, Polyhedron 8 (1989) 2003–2006.
- [33] D.-K. Hwang, Y. Chi, S.M. Peng, G.H. Lee, Organometallics 9 (1990) 2709-2718.
- [34] L.J. Farrugia, S.E. Rae, Organometallics 11 (1992) 196-206.
- [35] P.M. Fritz, K. Polborn, M. Steimann, M. Beck, Chem. Ber. 122 (1989) 889-891.
- [36] G.A. Koutsantonis, J.P. Selegue, J.G. Wang, Organometallics 11 (1992) 2704–2708
- [37] P. Mathur, A.K. Bhunia, C. Srinivasu, S.M. Mobin, J. Organomet. Chem. 670 (2003) 144–150.
- [38] M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis, Inorg. Synth. 21 (1982) 82.
- [39] W. Hieber, J. Gruber, Z. Anorg. Allg. Chem. 296 (1958) 91-103.
- [40] D.A. Lesch, T.B. Rauchfuss, Inorg. Chem. 20 (1981) 3583-3585.
- [41] SHELXL97 G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112-122.