J. Chem. Research (S),
1998, 494
J. Chem. Research (M),
1998, 2168–2174

Synthesis of Novel Butterfly-shaped Fe_2SeP and Fe_2SeAs Clusters *via* Reactions of $[Et_3NH][(\mu\text{-}RSe)(\mu\text{-}CO)Fe_2(CO)_6]$ with Some Electrophiles

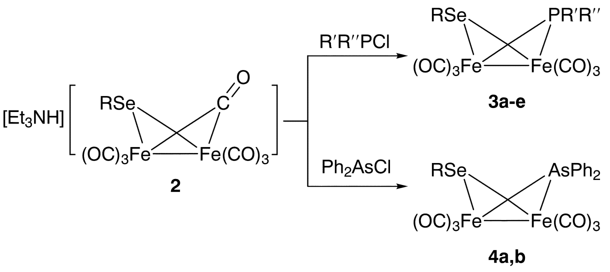
Li-Cheng Song,* Chao-Guo Yan, Qing-Mei Hu and Xiang-Dong Qin

Department of Chemistry, Nankai University, Tianjin 300071, China

Reactions of $[Et_3NH][(\mu\text{-}RSe)(\mu\text{-}CO)Fe_2(CO)_6$ with some phosphorus and arsenic chlorides afforded seven new butterfly-shaped Fe_2SeP and Fe_2SeAs clusters $(\mu\text{-}RSe)(\mu\text{-}R'R''P)Fe_2(CO)_6$ and $(\mu\text{-}RSe)(\mu\text{-}Ph_2As)Fe_2(CO)_6$, respectively.

Although the reactions of $[Et_3NH][(\mu\text{-}RS)(\mu\text{-}CO)Fe_2(CO)_6$ (**1**)[3] with P- and As-containing electrophiles have been previously studied and utilized in the synthesis of butterfly-shaped Fe_2SP and Fe_2SAs clusters, those of $[Et_3NH][(\mu\text{-}RSe)(\mu\text{-}CO)Fe_2(CO)_6]$ (**2**)[7] with P- and As-containing electrophiles to obtain the corresponding Fe_2SeP and Fe_2SeAs clusters have not been reported so far.

Recently, we found that $[Et_3NH][(\mu\text{-}RSe)(\mu\text{-}CO)Fe_2(CO)_6]$ (R = Ph, *p*-MeC_6H_4) (**2**), prepared from $Fe_3(CO)_{12}$, Et_3N and RSeH, reacted *in situ* with $PhPCl_2$, Ph_2PCl or Ph_2AsCl in THF or with PCl_3 in THF–Et_2O at room temperature to give butterfly-shaped Fe_2SeP clusters $(\mu\text{-}RSe)(\mu\text{-}R'R''P)Fe_2(CO)_6$ (**3a**–**e**) and Fe_2SeAs clusters $(\mu\text{-}RSe)(\mu\text{-}Ph_2As)Fe_2(CO)_6$ (**4a**–**b**) (Scheme 1 and Table 1).

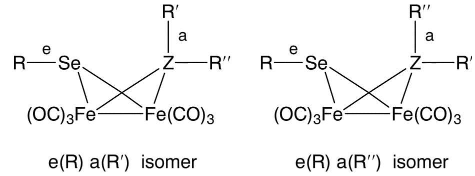


Scheme 1

Table 1 Yields of **3a**–**e** and **4a,b**

Product	R	R′	R″	Yield (%)
3a	Ph	Cl	Cl	23
3b	*p*-MeC_6H_4	Cl	Cl	22
3c	Ph	Cl	Ph	55
3d	*p*-MeC_6H_4	Cl	Ph	53
3e	*p*-MeC_6H_4	Ph	Ph	23
4a	Ph	—	—	21
4b	*p*-MeC_6H_4	—	—	27

In principle, clusters of the type $(\mu\text{-}RSe)(\mu\text{-}R'R''Z)Fe_2(CO)_6$, similar to $(\mu\text{-}RS)(\mu\text{-}R'R''Z)Fe_2(CO)_6$ (Z = P,[10] As[11]) would have two isomers, in which the R group is attached to the Se atom by an equatorial bond (Scheme 2), since other isomers in which the R group is attached to the Se atom by an axial bond have too strong steric repulsions between the two axial groups R and R′ or R and R″.



Scheme 2

However, for clusters **3a**,**b**,**e** and **4a**,**b** only one isomer exists since R′ = R″, which is in good agreement with the ^1H NMR signals of the *p*-Me substituent in **3b**, **3e** or **4b** being a singlet at δ 2.28, 2.27 and 2.29, respectively. Although **3c** and **3d** could have two isomers [for example, for **3d**, e(*p*-MeC_6H_4)a(Cl) and e(*p*-MeC_6H_4)a(Ph)], the ^1H NMR spectrum of the *p*-Me substituent in **3d** showed only a singlet at δ 2.34. This implies that **3c** and **3d** exist as either one isomer or as two isomers which undergo fast exchange on the ^1H NMR timescale.

We are grateful to the National Natural Science Foundation of China, the State Key Laboratory of Structural Chemistry and the State Key Laboratory of Elemento-Organic Chemistry for financial support of this work.

Techniques used: IR, ^1H NMR, mass spectrometry

Schemes: 3

References: 18

Received, 7th April 1998; Accepted, 5th June 1998
Paper E/8/02652A

References cited in this synopsis

3 D. Seyferth, D. P. Rauschke, W. M. Davis, M. Cowie and A. D. Hunter, *Organometallics*, 1994, **13**, 3834.
7 L.-C. Song, C.-G. Yan, Q.-M. Hu, R.-J. Wang, T. C. W. Mak and X.-Y. Huang, *Organometallics*, 1996, **15**, 1535.
10 L.-C. Song, Y. Li, Q.-M. Hu, R.-J. Wang, W.-J. Zhao, Y.-Q. Fan, S.-J. Zhang, X.-Q. Lu and G.-W. Li, *Chem. J. Chin. Univ.*, 1990, **11**, 154.
11 L.-C. Song, R.-J. Wang, Y. Li, H.-G. Wang and J.-T. Wang, *Acta Chim. Sin.*, 1990, **48**, 867.

---

*To receive any correspondence.