An Unusual Cyclopentaannulation Reaction: Thermolysis of an α,β-Unsaturated Fischer Carbene Complex Anchored on a $Fe_2(CO)_6(\mu\text{-}Se)_2$ Core

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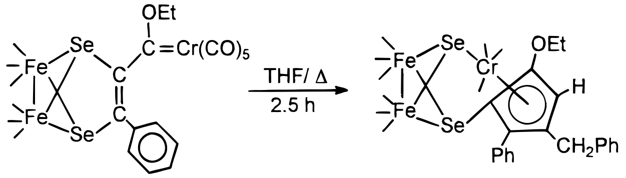
*Summary: An unusual annulation of a Fischer carbene complex anchored on a $Fe_2(CO)_6(\mu\text{-}Se)_2$ core is examined. Thermolysis of $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(Se)[(OEt)C{=}Cr(CO)_5]\}$ in THF yields an unusual annulated product, $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt))\}]$ (**1**), as characterized by IR and ^1H, ^{13}C, and ^{77}Se NMR spectroscopies, and its structure has been established by single-crystal X-ray diffraction.*

Introduction

Fischer carbene complexes of group 6 transition metals are valuable reagents in organic synthesis, these complexes are capable of reacting with alkynes to form a diverse array of structurally interesting compounds,[1] and the products obtained have been found to vary considerably depending on the metal employed and the ancillary ligands that are present in the complex.

Recently, we have observed that the homo- and mixed-chalcogenide compounds $Fe_2(CO)_6(\mu\text{-}EE')$ (where $E \neq E'$ and $E, E' = S, Se, Te$) readily add to the activated triple bond of alkynyl carbene complexes of the Fischer-type, $(CO)_5M{=}C(OEt)C{\equiv}CPh$[2] (where M = Cr or W). The metal−carbene fragment, a synthetically useful function which remains intact in the trimetallic adduct, $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(Se)[(OEt)C{=}Cr(CO)_5]\}$, offers many interesting possibilities of chemical modification of the organic appendage to the cluster. The structure of the adduct clearly showed a considerable proximity of the aromatic ring with the $Cr(CO)_5$ fragment. It was anticipated that the phenyl ring, placed *syn* to the metal−carbene fragment, could assist in removing a CO ligand from the metal pentacarbonyl unit and create a coordinatively unsaturated, reactive species which would trigger new reaction cascades or a stable, η^6-arene−metal-coordinated complex as obtained by Merlic.[3] The present report describes the structural elucidation of a novel product as testimony to the diversity of the new reaction pathways available to the parent adduct.

Scheme 1



Results and Discussion

The preparation and characterization of the starting materials have been described in detail earlier.[2] When a THF solution containing $[Fe_2(CO)_6Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ was heated under reflux in an argon atmosphere for 2.5 h, formation of a new, red-colored complex $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt))\}]$ was observed, which was isolated from the reaction medium by chromatography using silica gel TLC plates (Scheme 1).

The structural features of **1** were identified on the basis of IR and ^1H, ^{13}C, and ^{77}Se NMR spectroscopies, and its structure was confirmed by single-crystal X-ray diffraction. Red crystals of **1** were grown from hexane at −4 °C, and a single-crystal X-ray diffraction analysis was carried out. Its molecular structure is shown in Figure 1. The structure can best be described as consisting of a $(CO)_3Cr\{(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt))\}$ moiety attached to the Se atoms of the open butterfly unit of $Fe_2(CO)_6(\mu\text{-}Se)_2$. The Cr−Se bond distance, 2.625(1) Å, is somewhat long as compared to the Cr−Se bond distances in $[CrFe_2(CO)_{10}Se_4]$ (2.411(2) and 2.429(14) Å),[4] $[Cp(CO)_2Fe(\mu\text{-}Se_2)Cr(CO)_2Cp]$ (2.495(2) and 2.555-

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[1] For reviews on the synthetic applications of Fischer carbene complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (b) Dötz, K. H. *Angrew Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Dotz, K. H. In *Organometallics in Organic Synthesis*: *Aspects of a Modern Interdisciplinary Field*; tom Dieck, H., de Meijere, A., Eds.; Springer: Berlin, 1988. (d) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, MA, 1989. (e) Wulff, W. D. In *Advances In Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. (f) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5.

[2] (a) Mathur, P.; Ghosh, S.; Sarkar, A.; Satyanarayana, C. V. V.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 3536. (b). Mathur, P.; Ghosh, S.; Sarkar, A.; Satyanarayana, C. V. V.; Puranik, V. G. *Organometallics* **1997**, *16*, 4392.

[3] Merlic, C. A.; Xu, D.; Khan, S. I. *Organometallics* **1992**, *11*, 412.

[4] Mathur, P.; Sekar, P.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 142.

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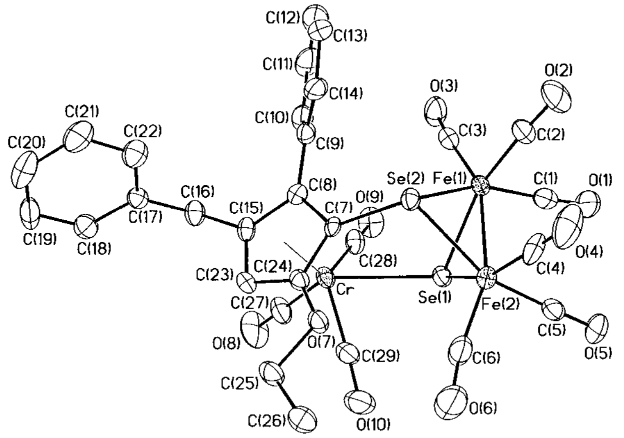

Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and bond angles (deg): Fe(1)−Fe(2) 2.5159(12), Fe(1)−Se(1) 2.3893(10), Fe(1)−Se(2) 2.3874(11), Cr−Se(1) 2.6250(10), Cr−C(7) 2.183(4), Cr−C(24) 2.243(5), Se(2)−C(7) 1.926(5),C(15)−C(16) 1.538(6); Fe(1)−Fe(2)−Se(2) 58.30(3), Fe(2)−Fe(1)−Se(2) 57.98(4), Fe(1)−Se(1)−Fe(2) 63.55(3), Fe(2)−Se(2)−Fe(1) 63.72(4), Se(1)−Fe(1)−Se(2) 84.01(4), Se(2)−Fe(2)−Se(1) 84.20(3), Cr−Se(1)−Fe(1) 110.57(4), Cr−Se(1)−Fe(2) 112.44(4), Se(1)−Cr−C(7) 82.87(12).

(2) Å),[5] and $[CpCr(CO)_2]_2Se_2$ (2.530 Å average).[6] The Fe−Fe and Fe−Se bond distances in **1**, 2.5159(12) and 2.3882 Å (average), respectively, are comparable with those observed in related molecules of the form $[(CO)_6Fe_2(\mu\text{-}SeXSe)]$: X = CH_2, 2.527(1) and 2.3741 (average) Å;[7] X = C(H)=C(Ph), 2.512(1) and 2.3837 (average) Å;[8] X = C(H)=C(C≡CMe), 2.507(2) and 2.3838 (average) Å;[9] and X = $[Pt(PPh_3)_2(Ph)C{=}C(H)]$, 2.534 and 2.365(2) (average) Å.[10] To the best of our knowledge, formation of a Cp ring followed by formation of a metal−Cp complex is unprecedented.

The product is clearly derived from two molecules of the starting compound from which one unit of $Fe_2(CO)_6(\mu\text{-}Se)_2$ is formally expelled. The mechanism, yet unclear, must also explain the presence of three additional hydrogen atoms in the product molecule.[11] If the hydrogens are abstracted from the solvent, involvement of a radical or carbene intermediate appears likely. The reaction seems to proceed well in polar solvents like THF or CH_3CN; compound **1** is not formed when benzene or toluene is used as the solvent.

Details of this unprecedented reaction are being investigated and will be reported in due course.

Experimental Section

General Procedures. All reactions and other manipulations were carried out under an argon or nitrogen atmosphere, using standard Schlenk techniques. Solvents were deoxygenated immediately prior to use. Reactions were monitored by FTIR spectroscopy and thin-layer chromatography. Infrared spectra were recorded on Nicolet-Impact 400 FTIR spectrometer as *n*-hexane solutions in a sodium chloride cell with a 0.1 mm path length. Elemental analyses were performed using a Carlo Erba 1106 automatic analyzer. ^1H, ^{13}C, and ^{77}Se NMR spectra were recorded on a Varian VXR 300S spectrometer in $CDCl_3$ at 25 °C. The operating frequency for ^{77}Se NMR was 57.23 MHz with a pulse width of 15 μs and a delay of 1.0 s. ^{77}Se NMR spectra were referenced to Me_2Se ($\delta = 0$ ppm).

Table 1. Crystallographic Data for $C_{29}H_{18}CrFe_2O_{10}Se_2$ (1)

formula	$C_{29}H_{18}CrFe_2O_{10}Se_2$
fw	848.05
space group	$P2_1/c$
a, Å	7.252(2)
b, Å	20.138(4)
c, Å	20.994(5)
α, deg	95.86(3)
V, Å^3	3051.4(10)
Z	4
cryst color, habit	red plate
D(calcd), g cm^3	1.846
λ(Mo Kα), cm^{-1}	37.29
T(max)/T(min)	1.52
diffractometer	Siemens P4
radiation	Mo Kα (λ = 0.710 73 Å)
$R(F)$, %^{a}	3.88
$R(wF^2)$, %^{a}	8.06

^{a} Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - Fc)|$.

Chromium hexacarbonyl, phenylacetylene, THF-d_8, and CH_3CN-d_3 were purchased from Aldrich Chemical Co. and used without further purification. The homochalcogenide iron carbonyl complex $Fe_2(\mu\text{-}Se_2)(CO)_6$,[12] α,β-unsaturated homochalcogenide carbene complexes $[(CO)_6Fe_2(\mu\text{-}SeCPh{=}C(Se)\text{-}[(OEt)C{=}Cr(CO)_5]\}$,[2] and alkynyl Fischer carbene complexes $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ (M = Cr, W)[13] were prepared as previously reported.

Preparation of 1. A THF solution of $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(Se)[(OEt)\ C{=}Cr(CO)_5]\}$(0.5 g, 0.63 mmol) was refluxed for 2.5 h. The color of the solution changed from red to brown. The solution was filtered through Celite to remove the insoluble material, and the resulting residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (9:1 v/v) yielded a trace amount of $Fe_3Se_2(CO)_9$ and a brown band of **1** (0.12 g, 24%).

IR [hexane, (ν(CO), cm^{-1}]: 2066 (vs), 2030 (vs), 2011(s), 1996 (s), 1989 (w), 1980 (w), 1950 (m). ^1H NMR (δ, ppm): 1.49 (3H, t, J = 6.9 Hz, CH_3), 3.1 (1H, d, part of an ABq, J = 15.3 Hz, −CH_2Ph), 3.77 (1H, d, part of an ABq, J = 15.3 Hz, −CH_2Ph), 3.88 (1H, dq, J = 6.9, 2.7 Hz, OCH_2), 4.1 (1H, cp), 6.64−7.68 (10H, m, 2C_6H_5). ^{13}C NMR (δ, ppm): 14.3 (CH_3, J_{C-H} = 128 Hz), 33.6 (CH_2Ph, J_{C-H} = 130 Hz), 67.2 (OCH_2, J_{C-H} = 143 Hz), 95.8 (*C*H in Cp ring), 116.3, 129.4, 131.8, 135.8 (*quat C* in phenyl and Cp ring), 126−129.7 (m, 2C_6H_5), 138.6 (Cp carbon atom attached with OEt), 149.5 (*C*Se), 208.2−209.4 (CO(Fe)), 234.7 ((CO)Cr), 237.1 ((CO)Cr). ^{77}Se NMR (δ, ppm): 206 and 395. Mp: 110−112 °C (decomp). Anal. Calcd (found) for $C_{29}H_{18}CrFe_2O_{10}Se_2$: C, 41.1 (41.3); H, 2.12 (2.30).

Crystal Structure Determination of 1. A red crystal of **1** was selected and mounted with epoxy cement to a glass fiber. Single-crystal X-ray data were collected on Siemens P4 diffractometer by using Mo Kα radiation. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2° ≤ 25°). Pertinent crystallographic data for **1** are summarized in Table 1. The

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(5) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Hecht, C.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1986**, *314*, 295.

(6) (a) Chen, W.; Goh, L. Y.; Sinn, E. *Organometallics* **1988**, *7*, 2020. (b) Goh, L. Y.; Wei, C.; Sinn, E. *J. Chem. Soc., Chem. Commun.* **1985**, 462.

(7) Mathur, P.; Manimaran, B.; Trivedi, R.; Hossain, M. M.; Arabatti, M. *J. Organomet. Chem.* **1996**, *515*, 155.

(8) Mathur, P.; Hossain, M. M. *Organometallics* **1993**, *12*, 2398.

(9) Mathur, P.; Hossain, M. M.; Rheingold, A. L. *J. Organomet. Chem.* **1996**, *507*, 187.

(10) Mathur, P.; Hossain, M. M.; Das, K.; Sinha, U. C. *J. Chem. Soc., Chem. Commun.* **1993**, 46.

(11) When the reaction was carried out in THF-d_8 or in CH_3CN-d_3, the ^1H NMR spectrum of complex **1** showed 20% and 33% deuterium incorporation, respectively.

(12) Mathur, P.; Chakrabarty, D.; Hossain, M. M.; Rashid, R. S.; Rugmini, V.; Rheingold, A. L. *Inorg. Chem.* **1992**, *31*, 1106.

(13) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47−51

systematic absences in the diffraction data for **1** are uniquely consistent for the reported space group. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semiempirical ellipsoid absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Conclusion

In summary, we have described the formation of a novel annulated product $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt))\}]$, in the thermolysis reaction of Fischer carbene complexes of the type $[(CO)_6Fe_2\{\mu\text{-}SeCPh{=}C(Se)(OEt)C{=}Cr(CO)_5]\}$ in a new annulated pathway. These results further augment the current perception that Fischer carbene reactivity can be diversely tailored by modification of the substituents at various positions of the key skeleton. The combination of designed cluster growth potential and multiple choices for altering functional appendages to the core metal cluster promises to provide a rich chemistry in the near future.

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Supporting Information Available: Crystallographic details including complete tables of atomic coordinates, bond lengths and bond angles, and anisotropic displacement parameters for **1** (6 pages). Ordering information is given on any current masthead page.

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