Journal of Organometallic Chemistry, 175(1979) C13—C16

Preliminary communication

PREPARATION AND REACTIVITY OF A SUBSTITUTED CYCLOHEPTATRIENYLTRICARBONYLIRON ANION, $[((C_6H_5)_3GeC_7H_6)Fe(CO)_3]^-$. *Endo*-PROTON ABSTRACTION FROM A COORDINATED CYCLOHEPTATRIENE

J.G.A. REUVERS and JOSEF TAKATS*
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 (Canada)
(Received April 9th, 1979)

Summary

Endo-proton abstraction from $(7\text{-}Ph_3GeC_7H_7)Fe(CO)_3$ has been achieved. The formed anion is fluxional and its reactivity resembles that of the unsubstituted analogue. The reaction with DCl produced exclusively two isomeric compounds and the selective formation of these two complexes is used to postulate the ground state structure of the anion.

Proton abstraction from polyolefinic ligands coordinated to a transition metal is beginning to emerge as a synthetically useful route toward the preparation of anionic organometallic complexes and frequently forms the initial step in the synthesis of new neutral organometallic species [1].

We and others have utilized the above outlined steps for the preparation of 7-substituted cycloheptatrienetricarbonyliron derivatives (eq. 1 and 2).

$$\underset{(I)}{(C_7H_8)Fe(CO)_3} \xrightarrow[THF]{RM} \underset{(II)}{[(C_7H_7)Fe(CO)_3]^-} M^+ + RH \qquad (1)$$

$$II \xrightarrow[R'X]{THF} (7\text{-}R'C_7H_7)Fe(CO)_3 + MX \qquad (2)$$

(RM = t-BuOK, n-BuLi, KH and $NaN(SiMe_3)_2$; R′ = $SiMe_3$, $SiEt_3$, $GeMe_3$, $GeEt_3$, $GePh_3$, COOMe, and $[(C_7H_7)M'(CO)_3]^+$; M′ = Fe, Cr, Mo, W)

However, in all cases so far reported the abstraction of the proton from the organic moiety occurs *exo* to the transition metal, i.e. from the face opposite to the one occupied by the metal atom. Electrophilic attack on the generated anion II by the Main Group IV reagents listed above also appears to proceed in an *exo* fashion. This was verified for a member of this series of compounds when an X-ray crystallographic study established an *exo* configuration for the $GeMe_3$ moiety [3a].

We now report that the substituted derivative, (7-$Ph_3GeC_7H_7$)$Fe(CO)_3$ (III) [3a] also undergoes proton abstraction to yield the corresponding substituted anion. Since this compound and the analogous (7-$MeOOCC_7H_7$)$Fe(CO)_3$, which can also be deprotonated [2c], are expected to contain *exo* substituents as well, they constitute the first examples of an *endo* proton abstraction from an organic moiety coordinated to a transition metal center.

Addition of III, dissolved in THF, to a slurry of one equivalent of t-BuOK in THF at ambient temperature resulted in the formation of a deep red solution. Solvent removal gave an extremely air-sensitive red solid. The infrared spectrum of this compound in THF solution exhibits two carbonyl absorption bands at 1938 and 1864 cm^{-1}. Although indicative of an anionic iron carbonyl species, these frequencies alone are by no means sufficient to prove the formation of the substituted anion $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$ (IV). Indeed, heterolytic cleavage of the Ge—C bond, a reaction already observed in the related (7-$Et_3GeC_7H_7$)$Fe(CO)_3$ by Behrens [2c], would give rise to the unsubstituted anion II, which also shows carbonyl absorptions at frequencies (1942 and 1868 cm^{-1}, respectively) very similar to those observed here. However, the ^1H NMR spectrum (Fig. 1) unambiguously establishes the formation of the substituted anion IV. We note the absence of any significant contribution to the δ 4.87 ppm resonance from the unsubstituted anion which exhibits a sharp singlet at δ 4.90 ppm at room temperature [3b]. Although chemical evidence suggests that II does indeed form in the reaction of III with t-BuOK, vide infra, the physical characteristics of the isolated compound clearly show that Ge—C bond cleavage constitutes but a minor component of the reaction. The assignments appearing in Fig. 1 were confirmed by double irradiation experiments on a more soluble and stable bis(triphenylphosphine)iminium salt. Noteworthy is the low field position of the resonance assigned to the protons 2,2'.

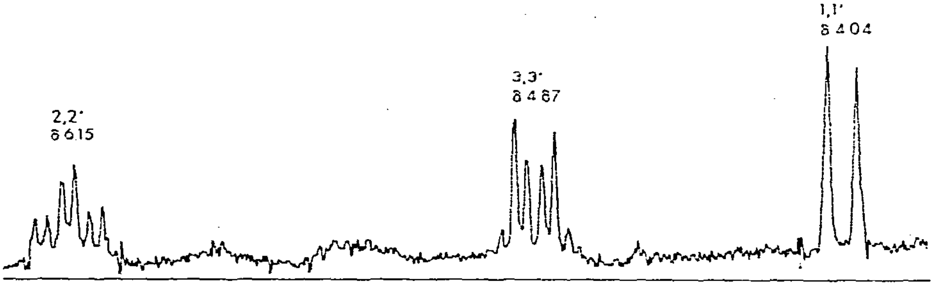


Fig. 1. 100 MHz ^1H NMR spectrum of $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$ PPN^+ in THF-d_8 at ambient temperature in the region 6.40 < δ (ppm) < 3.90.

The spectrum at room temperature would be consistent with a symmetrical structure for IV, but it more likely represents the time-averaged spectrum resulting from rapid ring-whizzing executed by the $Fe(CO)_3$ moiety. Such a rearrangement is known to be extremely facile in the unsubstituted anion both from theoretical predictions [4] and experimental evidence [3b]. The correctness of the latter proposal was verified by variable temperature ^{13}C NMR studies in THF-d_8. The resonances due to the ring carbon atoms in IV broaden and coalesce into the baseline at around −60°C. No further changes were observed down to −90°C. Unfortunately the great reactivity of the complex toward chlorinated solvents has so far precluded the extension of this study to lower temperatures, thus the low temperature limiting spectrum and the ground state structure of IV in solution remain elusive.

Preliminary experiments indicate that anion IV will undoubtedly display a chemistry as varied and rich as that of the parent unsubstituted complex. The chemical behaviour of IV seems to follow that of II, although differences in reactivity do occur. The reaction with Ph_3SnCl gives $(\eta^3\text{-}Ph_3GeC_7H_6)Fe(CO)_3\text{-}SnPh_3$ (V)*, a fluxional molecule containing an Fe—Sn bond and an allyl-bound cycloheptatrienyl ring, thus mirroring the reaction of II with Ph_3SnCl [3c]. We note that some $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ is formed in the above reaction as well.

However, no ring disubstituted complexes could be isolated from the reaction between IV and Me_3SiCl. Instead the carbon—carbon bonded dimeric species V was obtained**. Spectral features are consistent with dimerization through the C(7)—C(7) bond and the substitution of the Ph_3Ge moiety at the C(6) position. Oxidative dimerization of II, especially in reactions with organic halides, has been noted before [2b]. Most interesting results have been obtained from deuteration (or reprotonation) experiments. Only two isomeric compounds, $(3\text{-}Ph_3Ge, 7\text{-}DC_7H_6)Fe(CO)_3$ [7a] ***and $(6\text{-}Ph_3Ge, 7\text{-}DC_7H_6)Fe(CO)_3$(VIIb) **** are isolated in a 2/1 ratio by repeated fractional crystallization. Based on ^1H NMR spectral results more than 80% deuterium incorporation has occurred exclusively at the *exo*-7 position.

The selective formation of these products upon deuteration is interesting and can be used in the following manner in order to arrive at a prediction concerning the ground state structure of IV. Recently, Green et al. [5] have formulated some simple rules concerning nucleophilic addition to coordinated unsaturated hydrocarbon ligands in cationic organotransition metal complexes. The rationale behind the rules focuses upon the positive charge carried by the different carbon atoms of the coordinated organic moieties. Particularly in the case of small and highly charged nucleophiles the rates of addition are charge rather than orbitally controlled. Extending these observations to electrophilic attack by D^+, one would again expect the regioselectivity to be governed by the negative charge on the particular carbon atoms. For an η^3-bonded cycloheptatrienyl ligand this means that attack by D^+ should preferentially occur at the terminal carbon atoms of the allyl part of the seven-membered ring. Based on this assumption and the product distribution observed above the dominant solution structure of IV can be deduced as IVa (eq. 3). As can be seen in eq. 3 attack by D^+ at carbon atom 1 of the anion will produce the $6\text{-}Ph_3Ge$ isomer, VIIb, whereas attack on the 3-position will yield the $3\text{-}Ph_3Ge$ isomer, VIIa, respectively.

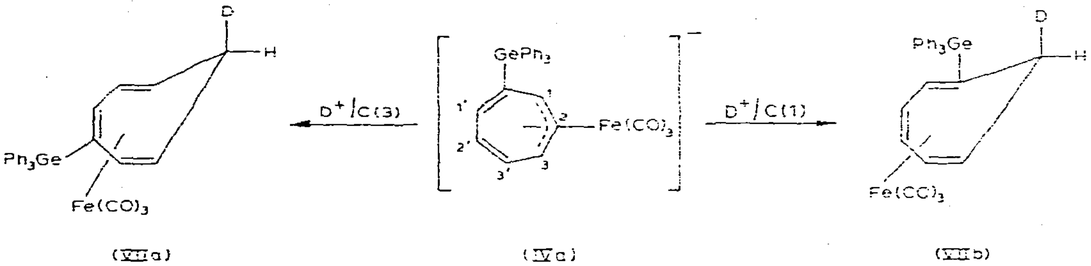
---

* ^1H NMR, δ (ppm) in C_6D_6: 4.38 (H(3,3′)), 4.69 (H(2,2′)), 5.90 (H(1,1′)).

** ^1H NMR, δ (ppm) in C_6D_6: 2.28 (H(7)), 2.54 (H(4)), 2.73 (H(1)), 4.48—4.58 (H(2,3), 6.13 (H(5)).

*** ^1H NMR, δ (ppm) in CS_2: 2.40 (H(7)), 2.94 (H(4)), 3.28 (H(1)), 4.82 (H(2)), 5.15 (H(6)), 5.75 (H(5)).

**** ^1H NMR, δ (ppm) in CS_2: 2.42 (H(7)), 3.01 (H(4)), 3.28 (H(1)), 5.15—5.30 (H(2,3)), 6.10 (H(5)).



(3)

We are attempting to grow single crystals of IV in order to verify the above prediction by X-ray crystallography. The reactivity of IV towards other electrophiles is also being investigated and will be reported in due course.

Acknowledgement

We would like to thank the National Research Council of Canada and the University of Alberta for financial support of this research and the Killam Foundation for a postgraduate fellowship (JGAR).

References

1 See, for example:
(a) W.S. Trahanowsky and R.J. Card, J. Amer. Chem. Soc., 94 (1972) 2897; (b) J.W. Kang and P.M. Maitlis, J. Organometal. Chem., 30 (1972) 127; (c) J.W. Johnson and P.M. Treichel, J. Chem. Soc., Chem. Commun., (1976) 688; (d) J.T. Bamberg and R.G. Bergman, J. Amer. Chem. Soc., 99 (1977) 3173; (e) A.N. Nesmeyanov, N.A. Ustynyuk, L.G. Makarova, S. Andre, Yu.A. Ustynyuk, L.N. Novikova and Yu.N. Luzikov, J. Organometal. Chem., 154 (1978) 45; (f) H. Maltz and B.A. Kelly, J. Chem. Soc., Chem. Commun., (1971) 1398.
2 (a) L.K.K. Li Shing Man and J. Takats, J. Organometal. Chem., 117 (1976) C104; (b) G. Deganello, T. Boschi and L. Toniolo, J. Organometal. Chem., 97 (1975) C46; (c) H. Behrens, K. Geibel, R. Kellner, H. Knöchel, M. Moll and E. Sepp, Z. Naturforsch. B, 31 (1976) 1021.
3 (a) C.S. Day, V.W. Day, G. Deganello, L.K.K. Li Shing Man, J.G.A. Reuvers and J. Takats, manuscript in preparation; (b) J. Henderson-Lypkie and J.G.A. Reuvers, unpublished observations; (c) J.G.A. Reuvers, J. Takats and V.W. Day, manuscript in preparation.
4 P. Hoffman, Z. Naturforsch. B, 33 (1978) 251.
5 S.G. Davies, M.L.H. Green and D.M.P. Mingos, Tetrahedron, 34 (1978) 3047.