Inorganica Chimica Acta, 53 (1980) L25–L27
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Preparation and Alkylation Reactions of $K^+[(CO)_4FeSi(CH_3)_3]^-$; Reductive Elimination of Tetramethylsilane from Isolable $(CO)_4FeRSi(CH_3)_3$ Complexes

ANDREW J. BLAKENEY and J. A. GLADYSZ*

Department of Chemistry, University of California, Los Angeles, Calif, 90024, U.S.A.

Received September 8, 1980

The increasingly recognized unique reactivity modes available to transition metal trialkylsilanes [1] have prompted us to synthesize new organometallic compounds containing the trimethylsilyl group [2]. Objectives include the development of new metal-carbon bond forming reactions, and clarification of the mechanistic steps involved in the catalytic hydrosylation of organic molecules [1]. In this communication, we report (a) the synthesis of a new transition metal anion $K^+[(CO)_4FeSi(CH_3)_3]^-$ (*1*), which can be alkylated to yield isolable $(CO)_4FeRSi(CH_3)_3$ complexes (*2*), and (b) the facile reductive elimination of $RSi(CH_3)_3$ from *2* when R = CH_3 or $CH_2H_6H_5$. The latter event is of particular significance, since the key postulated step in catalytic olefin hydrosilylation – alkyl silane elimination from a $L_nM(R)(SiR_3)$ intermediate [3, 4] – has not previously been directly observed.

When a THF slurry of $K_2^+[(CO)_4Fe]^=$ [5] was reacted for 0.5 hr at 0 °C with 1 equiv. of $(CH_3)_3SiBr$, a new iron silane formed. Ether extraction of the reaction residue yielded a crude product (*ca.* 50%) whose spectral properties (NMR, acetone-d_6: ^1H, δ 0.34; ^{13}C, 221.3, 8.0 ppm. IR (THF, cm^{-1}): 1980 m, 1887 s, 1872 s, 1832 m) suggested it to be $K^+[(CO)_4FeSi(CH_3)_3]^-$ (*1*: Scheme 1). Metathesis with $[(C_6H_5)_3P]_2N^+Cl^-$ (PPN^+Cl^-) afforded white, air stable $PPN^+[(CO)_4FeSi(CH_3)_3]^-$ whose spectral properties were similar to *1* and analytical properties (*Anal.* Calcd. for $C_{43}H_{39}FeNO_4P_2Si$: C, 66.24; H, 5.04; Fe, 7.16; N, 1.80; P, 7.95; Si, 3.60. Found: C, 65.95; H, 5.21; Fe, 6.86; N, 2.02; P, 7.73; Si, 3.24%) unequivocally established its composition. *1* could be independently prepared by treatment of $(CO)_4FeHSi(CH_3)_3$ [6] with KH. Also, the reaction of *1* (petroleum ether slurry) with $(CH_3)_3SiBr$ yielded the known compound $(CO)_4Fe[Si(CH_3)_3]_2$ [7].

Ether slurries of *1* reacted with CH_3SO_3F and $CH_3CH_2SO_3F$ within 2 minutes at 0 °C. After filtra-

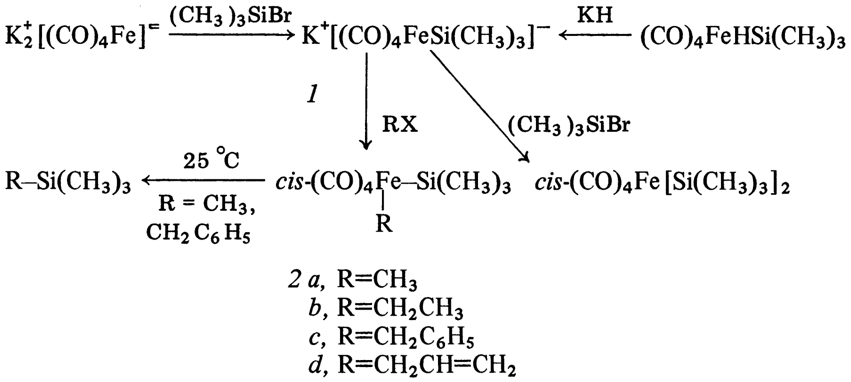
TABLE I. Spectroscopic Properties of *cis*-$(CO)_4FeRSi(CH_3)_3$ Complexes Prepared.

R	^1H NMR (δ)	^{13}C NMR[a] (ppm)	IR (cm^{-1}, hexane)
CH_3 (*2a*)	0.34 (s, 9H) 0.03 (s, 3H)[c,d]	210.3, 206.5, 204.8 (*C*O's)[b] 5.5 (Si*C*H_3), −12.7 (Fe*C*H_3)[c,e]	2088 m, 2027 s 2000 vs
CH_2CH_3 (*2b*)	1.31 (m, 3H) 1.13 (m, 2H) 0.33 (s, 9H)[c,d]	211.1, 206.0, 205.3 (*C*O's)[b] 6.8 (Fe*C*H_2–), 5.4 (Si*C*H_3)[c,e,f]	2086 m, 2023 s, 1997 vs
$CH_2C_6H_5$ (*2c*)	7.28–6.95 (m, 5H) 2.45 (s, 2H) 0.40 (s, 9H)[e,g]	211.7, 205.6, 202.7 (*C*O's)[b] 150.9, 125.0 (C_6H_5)[e] 16.0 (Fe*C*H_2–), 5.7 (Si*C*H_3)[e,g,h]	2085 m, 2028 s, 1998 vs
$CH_2CH{=}CH_2$ (*2d*)	6.57–5.77 (m, 1H) 5.03 (d of m), overlapping with 4.88 (d of d, J = 2, 10 Hz), 2H total 1.86 (d, J = 9 Hz, 2H) 0.37 (s, 9H)[e,g]	210.7, 205.8, 204.3 (*C*O's)[b] 145.4, 109.5 (*C*=*C*), 15.1 (Fe*C*H_2–), 5.5 (Si*C*H_3)[c,e]	2085 m, 2028 s, 2003 vs

[a] In the presence of $Cr(acac)_3$. [b] The low field carbonyl resonance is approximately twice as intense as the other two. [c] In toluene-d_8 at −20 °C. [d] Referenced to $CH_3C_6H_5$ at δ 2.07. [e] Referenced to $(CH_3)_4Si$. [f] $FeCH_2CH_3$ resonance obscured by toluene-d_8; in CD_2Cl_2 (−20 °C), resonances appear at 211.3, 206.4, 205.7, 22.0, 6.7, and 5.6 ppm. [g] In benzene-d_6 at ambient probe temperature. [h] Some phenyl resonances obscured by benzene-d_6.

---

*Author to whom correspondence should eb addressed.



Scheme 1. Formation and Reactions of *1* and *2*.

tion, solvent removal, and distillation at 25 °C and $<10^{-3}$ mm, iron alkyls *2a* and *2b* (Scheme 1) were isolated as colorless liquids in 46 and 56% yields, respectively. Benzyl bromide reacted similarly with *1* (0.5 hr, 25 °C) to yield *2c* (75%). The reaction of allyl bromide with *1* (7 minutes, 25 °C) afforded the iron allyl *2d*, which underwent partial decomposition upon distillation. The spectral properties of *2a–d* (Table I) are in full accord with the assigned structures. In particular, the ^{13}C NMR spectra show three carbonyl absorptions in a 2:1:1 height ratio, as would be expected of non-fluxional *cis* geometric isomers [8].

2a–d are all air sensitive and undergo decomposition at room temperature over periods ranging from 6 hr (*2d*) to 5–6 days (*2c*). The decompositions of *2b* and *2d* are complex and still under study: volatile $RSi(CH_3)_3$ species are not produced in appreciable quantities (<5%), and *2d* does not appear to give rise to a π-allyl $Fe(CO)_3SiR_3$ complex [9]. However, *2a* clearly yields $(CH_3)_4Si$ (identified by ^{1}H NMR and GLC) as the only proton-containing decomposition product and $(CH_3)_3SiCH_2C_6H_5$ is obtained in 63% GLC yield from *2c*; significant amounts (<1%) of bibenzyl are not formed.

The preceding results are noteworthy in several respects. First, osmium homologs of *1* and *2* were prepared in important earlier work by Stone and Knox [10]. However, no observation of $RSi(CH_3)_3$ elimination was reported. Secondly, $Fe(CO)_5$ has been previously demonstrated to be an effective olefin hydrosilylation catalyst precursor [4, 6, 11]. Thus species closely related to *2* may under certain conditions be *bona fide* catalytic intermediates. However, decomposition pathways other than simple reductive elimination are available to $(CO)_4FeRSi(CH_3)_3$ complexes; previously we noted that $(CO)_4Fe[(CH(C_6H_5)OSi(CH_3)_3]Si(CH_3)_3$ undergoes facile iron–carbon bond homolysis at room temperature [1]. Dimerization of resulting stabilized $\cdot[CH(C_6H_5)OSi(CH_3)_3]$ radical occurs. Collman has observed that $(CO)_4FeRR'$ complexes thermally decompose to ketones [12], implying that alkyl group migration to coordinated CO precedes reductive elimination. The fact $Fe(CO)_5$-based olefin hydrosilylation catalysts often afford appreciable quantities of 'abnormal' products such as vinyl silanes may be relevant to these alternative decomposition modes.

In summary, this study has made available two new types of iron–$Si(CH_3)_3$ complexes for which useful applications can be envisioned. Finally, since numerous examples exist of M–H bond addition to olefins [13] and several L_nMHSiR_3 species have been prepared by $HSiR_3$ addition to metals [6, 14] direct precedent now exists for all steps postulated to occur in catalytic olefin hydrosilylation.

Acknowledgements

We thank the National Science Foundation (NSF) for support of this research. FT NMR spectrometers employed in this study were obtained via NSF departmental instrumentation grants.

References

1 D. L. Johnson and J. A. Gladysz, *J. Am. Chem. Soc.*, *101*, 6433 (1979).
2 A. J. Blakeney and J. A. Gladysz, *J. Organometal. Chem.*, in press.
3 J. L. Speier, *Adv. Organometal. Chem.*, *17*, 407 (1979).
4 J. F. Harrod and A. J. Chalk, 'Hydrosilation Catalyzed by Group VIII Complexes', in 'Organic Syntheses via Metal Carbonyls", Vol. II, I. Wender and P. Pino, Eds., John Wiley and Sons, New York, 1977, pp. 673 - 704.
5 J. A. Gladysz and W. Tam, *J. Org. Chem.*, *43*, 2279 (1978).
6 M. A. Schroeder and M. S. Wrighton, *J. Organometal. Chem.*, *128*, 345 (1977).

7 W. Jetz and W. A. G. Graham, *J. Organometal. Chem., 69,* 383 (1974).

8 L. Vancea, R. K. Pomeroy and W. A. G. Graham, *J. Am. Chem. Soc., 98,* 1407 (1976); R. K. Pomeroy, L. Vancea, H. P. Calhoun and W. A. G. Graham, *Inorg. Chem., 26,* 1508 (1977).

9 J. W. Connolly and C. D. Hoff, *J. Organometal. Chem., 160,* 467 (1978).

10 S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. (A),* 3147 (1970).

11 A. N. Nesmeyanov, R. K. Friedlina, E. C. Chukovskaya, R. G. Petrova and A. B. Belyavsky, *Tetrahedron, 17,* 61 (1962).

12 J. P. Collman, S. R. Winter and D. R. Clark, *J. Am. Chem. Soc., 94,* 1778 (1972); W. O. Siegl and J. P. Collman, *ibid., 94,* 2516 (1972)

13 H. D. Kaesz and R. B. Saillant, *Chem. Rev., 72,* 231 (1972).

14 W. Jetz and W. A. G. Graham, *Inorg. Chem., 10,* 4 (1971) and references therein.

Inorganica Chimica Acta, 53 (1981) L28

Novel Reaction of Coupling of π-Allyl and π-acetylene Ligands Coordinated to Metal Atom

Z. L. LUTSENKO, A. V. KISIN, M. G. KUZNETSOVA, A. A. BEZRUKOVA, V. S. KHANDKAROVA and A. Z. RUBEZHOV*

Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Moscow 117813, ul Vavilova, 28, U.S.S.R.

Received September 8, 1980

Numerous reactions of acetylenes resulting in the formation of cyclobutadiene [1] and arene ligands [2] are well reviewed in the literature. Information concerning the formation of cyclopentadienyl compounds by reactions of alkynes with transition-metal complexes is restricted to several examples [3].

In our study of the reactivitiy of cationic allyl-arene complexes of Ruthenium with different neutral ligands we have observed a novel reaction of intramolecular condensation of π-allyl and π-tolane ligands abbording a π-arene-π-cyclopentadienyl derivative of Ruthenium.

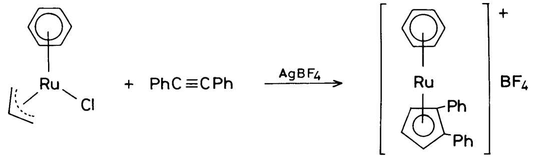
The reaction of π-C_3H_5-π-C_6H_6-RuCl with tolane in acetone in inert atmosphere under ambient conditions in the presence of silver tetrafluoroborate gave a stable pale yellow crystalline solid which proved not to be π-C_6H_6-π-C_3H_5-Ru-π-C_2Ph_2 as expected.

The Raman spectrum of the product obtained showed the absence of the band corresponding to coordinated diphenylacetylene.

The ^{1}H NMR spectrum of the compound (in CD_3CN) consists of a multiplet at δ 7.4 ppm corresponding to phenyl protons, a single resonance of protons of π-arene ring at δ 6.13 ppm, a doublet at δ 5.76 ppm (J_{H-H} 2.5 Hz) and a triplet at δ 5.52 ppm. The intensity ratio of bands (10:6:2:1) indicates that the reaction is accompanied by the loss of two hydrogen atoms.

The ^{13}C NMR spectrum* (in CD_3CN) exibits a set of signals corresponding to phenyl carbon atoms in the region of 128.3–129.9 ppm, a singlet at δ 101.7 ppm and three doublets at δ 87.7, 81.2 and 78.5 ppm. The low field doublet may be assigned to the carbon atoms of π-arene ligand while the other two must represent resonances of π-allyl ligand. However doublet splitting of these signals shows that these atoms are bonded only to one proton while terminal allylic carbon atoms are bonded to two hydrogen atoms.

All these results indicate that the product obtained is π-benzene-π-(1,2-diphenylcyclopentadienyl)-Ruthenium-tetrafluoroborate**, *i.e.* condensation of π-allyl ligand with tolane occurred:



Conclusive proof of the structure was obtained from X-ray crystallographic investigation***. Preliminary results demonstrate that the reaction may be of general interest and analogous complexes have been prepared for other platinum metals.

References

1 L. V. Rybin, in A. N. Nesmeyanov and K. A. Kocheshkov (Eds), ‘Methods of Organo-Element Chemistry. The Types of Organometallic Compounds of Transition Metals’, V. 2, p. 547–553, Nauka, Moscow (1975).
2 N. A. Vol’kenau, in A. N. Nesmeyanov and K. A. Kocheshkov (Eds), ‘Methods of Organo-Element Chemistry. The Types of Organometallic Compounds of Transition Metals’, p. 166–168, Nauka, Moscow (1976).
3 W. Hübel and R.Merenyi, *J. Organometal. Chem., 2,* 213 (1964); T. R. Jack, C. J. May and J. Powell, *J. Am. Chem. Soc., 99,* 4707 (1977); M. I. Bruce, R. C. F. Gardner and F. G. A. Stone, *J. Chem. Soc. Dalton,* 906 (1979).

---

*Author to whom correspondence should be addressed.

*Doublet structure of ^{13}C signals is observed in Off Resonance Decoupled spectra.

**The formulation is supported by elemental analysis.

***Results will be published later.