Journal of Organometallic Chemistry, 73 (1974) C10—C12

Preliminary communication

ACTIVATION OF IRON-COORDINATED ARENES TOWARD THE ATTACK OF CARBON, NITROGEN, AND OXYGEN NUCLEOPHILES

JOHN F. HELLING* and GORDON G. CASH

Department of Chemistry, University of Florida, Gainesville, FL 32611 (U.S.A.)

(Received March 22nd, 1974)

Summary

Functionally-substituted carbon nucleophiles undergo addition to arenes coordinated to positive iron, but nitrogen and oxygen nucleophiles abstract α protons from iron-coordinated methylated arenes.

Previous work in this laboratory has shown that arenes are activated toward the addition of nucleophiles by coordination to positive iron in bis-areneiron(II) salts [1, 2]. From RLi reagents (R = alkyl, aryl, vinyl) are produced neutral di-adducts and cationic mono-adducts depending on the stoichiometry.

We now report that other carbon nucleophiles bearing functional groups undergo facile addition to iron-coordinated arenes to give mono-adducts. However, with nitrogen and oxygen nucleophiles the products result from initial proton abstraction from the methyl groups of methylated iron-coordinated arenes.

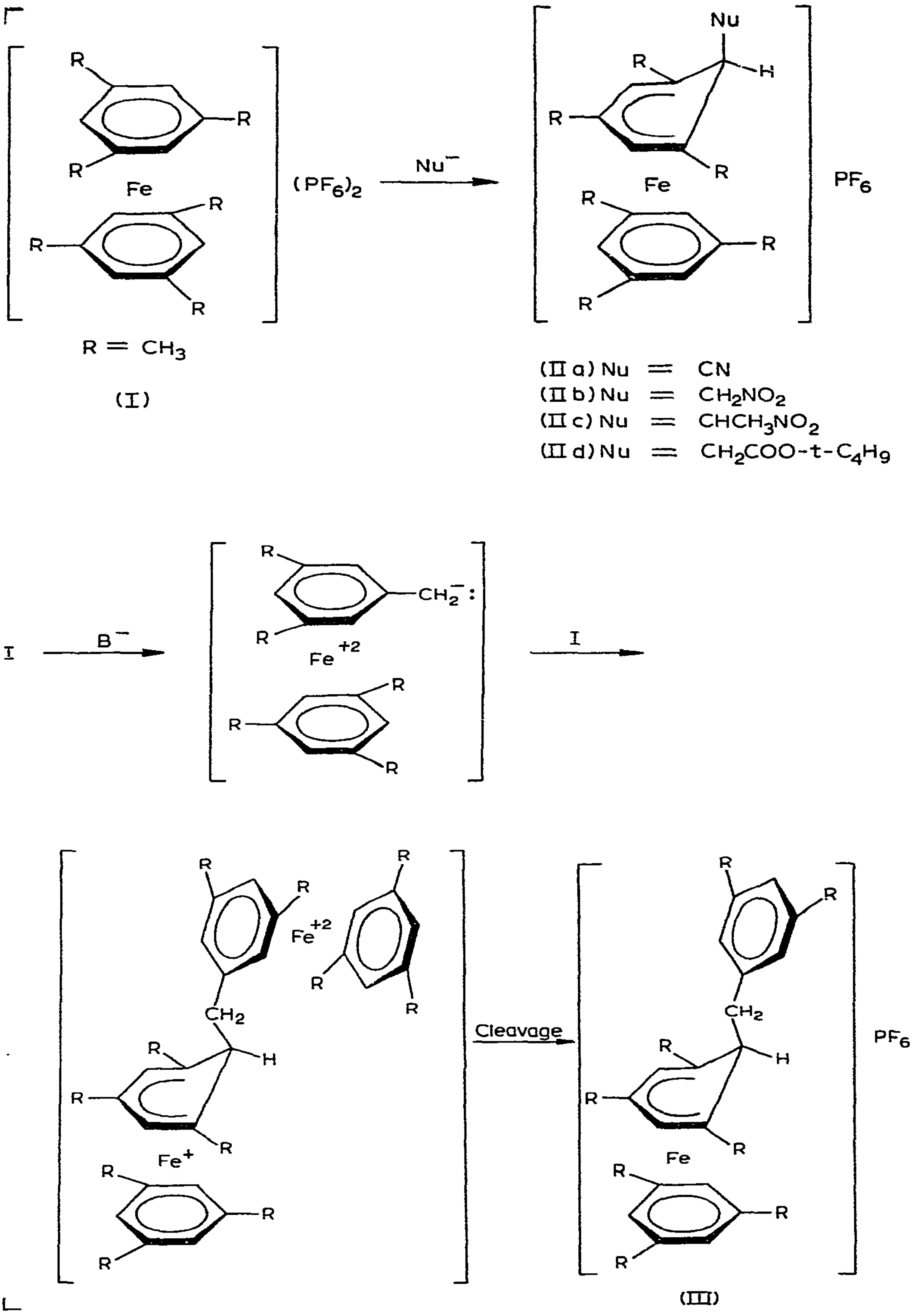
When bis(mesitylene)iron(II) hexafluorophosphate (I) was stirred with KCN in acetone at 25° for 30 minutes an 83% yield of mono-adduct IIa was produced. Likewise I and $LiCH_2NO_2$ in CH_3NO_2 gave IIb in 52% yield after 5 minutes. An 84% yield of IIc was obtained from $LiCHCH_3NO_2$ and I in nitroethane in 1 minute. From I and $LiCH_2COO\text{-}t\text{-}C_4H_9$ in ether there resulted 48% of IId in 1 hour. The structure assignments are supported by IR and NMR spectra and by elemental analyses. In each case the absence of a C—H stretching frequency in the 2700—2800 cm^{-1} region of the infrared is consistent with *exo* addition [3]. Attempts to form the corresponding di-adducts have been unsuccessful.

Oxidation of IIa—IId with ceric ammonium nitrate gave 1/1 mixtures of mesitylene and the appropriate substituted mesitylene based on NMR spectra. The substituted mesitylenes derived from IIa, IIb and IId were isolated in yields of 53, 45, and 50%, respectively.

Several oxygen and nitrogen nucleophiles reacted with I (see Table 1) to

---

*To whom correspondence should be addressed.



$R = CH_3$

(I)

(IIa) $Nu = CN$
(IIb) $Nu = CH_2NO_2$
(IIc) $Nu = CHCH_3NO_2$
(IId) $Nu = CH_2COO\text{-}t\text{-}C_4H_9$

(III)

TABLE 1

Nucleophile source	Solvent	Yield of III (%)
$LiNH_2$	Tetrahydrofuran	11
$LiN(CH_3)_2$	Benzene	34
$NaN[Si(CH_3)_3]_2$	Benzene	36
$LiOCH_3$	Methanol	21
$KO\text{-}t\text{-}C_4H_9$	Tetrahydrofuran	19

produce the same mono-adduct III. The structure of III (m.p. 168—170°) is supported by its elemental analysis, infrared spectrum, and NMR spectrum in acetone-d_6 (τ 3.23, broad singlet, 1 proton; 3.53, broad singlet, 2; 4.33, singlet, 3 5.80, singlet, 2; 7.03, poorly resolved triplet, 1, J 6 Hz; 7.43, singlet, 3; 7.60, singlet, 9; 7.82, singlet, 6; 8.22, doublet, 2, J 6 Hz; 8.48, singlet, 6). Its ultraviolet spectrum in methanol [λ_{max} (ϵ): 237 (21900), 290 (5400), 350 (2750), 403 (541)] is similar to those of other mono-adducts [4]. A peak representing the fragment $C_{18}H_{22}$ (m/e 238) is found in its mass spectrum.

Presumably the formation of III is a consequence of initial attack of a base on an α proton of I which could be followed by carbanion addition to another ion I and finally fragmentation.

As further evidence of α-proton activation we have found that bis(hexamethylbenzene)iron(II) bromide undergoes rather rapid deuterium exchange in D_2O catalyzed by triethylenediamine. Exchange of the 36 protons per cation is 75% complete in 90 minutes at room temperature and 94% complete in 24 h based on NMR and mass spectral measurements. Uncoordinated hexamethylbenzene gave no detectable proton exchange (mass spectrometric analysis) after 20 h at room temperature in a 95% dimethylformamide—5% D_2O solvent mixture containing triethylenediamine. Similar activation of α-methyl protons toward base attack has been reported for metal-coordinated duroquinone (M = Co, Rh, Ir) [5] and pentamethylcyclopentadienyl (M = Rh) ligands [6].

Acknowledgement

Partial support of this work by the Research Corporation is gratefully acknowledged.

References

1 J.F. Helling and D.M. Braitsch, J. Amer. Chem. Soc., 92 (1970) 7207.
2 J.F. Helling and D.M. Braitsch, J. Amer. Chem. Soc., 92 (1970) 7209.
3 P.H. Bird and M.R. Churchill, Chem. Commun., (1967) 777.
4 D.M. Braitsch, Ph. D. dissertation, University of Florida, 1971.
5 D.W. Slocum and T.R. Engelmann, J. Amer. Chem. Soc., 94 (1972) 8596.
6 J.W. Kang and P.M. Maitlis, J. Organometal. Chem., 30 (1971) 127.