Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

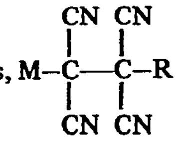
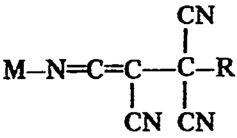
Preliminary communication

The diversity of behavior of tetracyanoethylene toward transition metal–carbon σ-bonded complexes

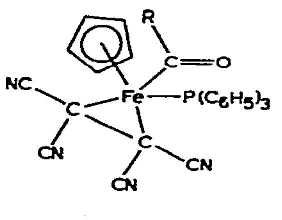
SOPHIA R. SU and ANDREW WOJCICKI

The McPherson and Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

(Received June 15th, 1971)

Transition metal alkyls of the type π-$C_5H_5Fe(CO)_2R$, π-$C_5H_5Cr(NO)_2R$, and π-$C_5H_5Mo(CO)_2(L)R$ react with tetracyanoethylene (TCNE) to give the corresponding 1,2- and/or 1,4-addition products,  $M{-}\underset{CN}{\overset{CN}{C}}{-}\underset{CN}{\overset{CN}{C}}{-}R$ (provisional formulation) and  $M{-}N{=}C{=}\underset{CN}{C}{-}\underset{CN}{\overset{CN}{C}}{-}R$, respectively[1]. We now wish to report that the nature of products from such reactions can change markedly upon suitable replacement of ancillary ligands or upon introduction of unsaturation into the hydrocarbon moiety R.

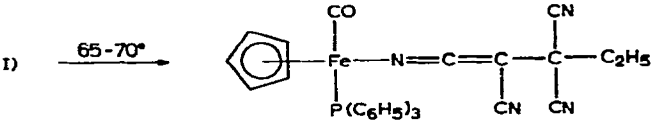
The reaction of TCNE in benzene with an equimolar amount of π-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$, also in benzene, at 5–10° produces an instantaneous color change from orange to dark green. Removal of the solvent after ca. 15 min and chromatography on alumina leads to the isolation (70–75%) of a dark green solid which, on the basis of the chemical analyses and its IR (no terminal ν(CO); ν(CN), 2195 (s, sharp), 2217 (sh); acyl ν(CO), 1651 (s), 1618 (sh) cm^{-1}; CH_2Cl_2 soln) and ^1H NMR spectra (π-C_5H_5, τ 4.83 (doublet), J = 1.0 Hz; CH_3, τ 7.18 (singlet)) is designated as π-$C_5H_5Fe[P(C_6H_5)_3](COCH_3)(C_6N_4)$ (I, R = CH_3). Similar, very rapid reactions occur with other π-$C_5H_5Fe(CO)(L)R$ ($L = P(C_6H_5)_3$, $R = C_2H_5$ or n-C_3H_7; $L = P(n\text{-}C_4H_9)_3$, $R = CH_3$; $L = P(OC_6H_5)_3$, $R = CH_3$) compounds. However, π-$C_5H_5Fe(CO)(L)CH_2C_6H_5$ ($L = P(C_6H_5)_3$ or $P(n\text{-}C_4H_9)_3$) afford keteniminato complexes, π-$C_5H_5Fe(CO)(L)[N{=}C{=}C(CN)C(CN)_2CH_2C_6H_5]$, instead.



(I)

The aforementioned "carbonyl insertion" reactions are noteworthy, since, apart from CO, which requires vigorous conditions[2], TCNE represents the only reagent capable of effecting an M(CO)(R) → M(COR) intramolecular conversion in substituted complexes of the type π-$C_5H_5Fe(CO)(L)R$. This remarkable reactivity may be best ascribed to strong electrophilic properties of the cyanoolefin TCNE[3].

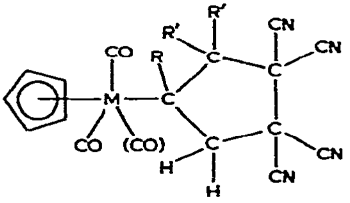
Thermal treatment of (I, R = C_2H_5) at 65–70° for 1–2 h, followed by chromatography on alumina, affords (II) in 30% yield:



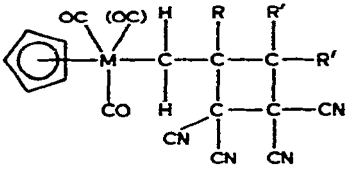
(II)

Whether this apparent transfer of C_2H_5 from CO onto a coordinated TCNE proceeds inter-, or intramolecularly is yet to be determined.

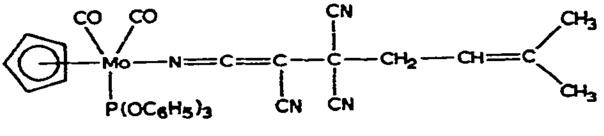
The reaction of π-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'_2$ or π-$C_5H_5Mo(CO)_3CH_2C(R){=}CR'_2$ (R = CH_3, R' = H; R = H, R' = CH_3) with TCNE in THF or CH_2Cl_2 at 25° for 5–30 min yields (50–95%) yellow solids which analyze as 1/1 adducts of the two reactants. Primarily on the basis of the ^1H NMR spectra of π-$C_5H_5M(CO)_xCH_2C(R){=}CR'_2\cdot$TCNE having R = CH_3 and R' = H (M = Fe, $x = 2$: π-C_5H_5, τ 4.86; CH_3, τ 8.32; CH_2, AB quartet with τ 6.98 and 6.62, $J = 14.5$ Hz; M = Mo, $x = 3$: π-C_5H_5, τ 4.14; CH_3, τ 8.16; CH_2, AB quartet with τ 6.80 and 6.32, $J = 15$ Hz) we favor structures derived from 1,3-[4] (III) rather than 1,2-addition (IV) of TCNE to C–C bonds★. By contrast, π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}C(CH_3)_2$ and TCNE react very slowly (~ 50 h) in CH_2Cl_2 at 25° to give a direct (1,4) insertion product (V). It appears that the pronounced inhibition and a different course of this reaction are due to replacement of CO with a bulky phosphite ligand.



(III)



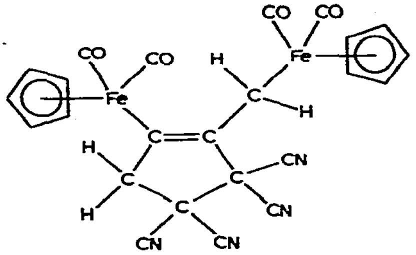
(IV)



(V)

★*Note added in proof.* We have now learned that cyclopentadienyliron dicarbonyl allyl–TCNE complexes have been prepared independently and formulated identically by Professor M. Rosenblum and Dr. W.P. Giering; M. Rosenblum, private communication.

The 2-alkynyls π-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ (R = CH_3 or $CH_2Fe(CO)_2(\pi$-$C_5H_5)$) also react with TCNE in THF, CH_2Cl_2 or CH_3CN at 25° to give 1/1 addition compounds. The IR spectrum of the product from the dimetallic π-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(\pi$-$C_5H_5)$ and TCNE exhibits four ν(CO) bands (2034 (vs), 2008 (s), 1979 (vs), and 1950 (s) cm^{-1}; CH_2Cl_2 soln); the corresponding ^1H NMR spectrum shows π-C_5H_5 resonances at τ 4.88 and 4.72 and two different CH_2 signals, both triplets (J = 1.2 Hz), at τ 7.40 and 6.50. From these data, and by analogy with the known behavior of the same iron complex toward SO_2[5] and C_6H_5NSO[6], we propose structure (VI) for this adduct. A similar ring structure, consistent with the spectral data, is assigned to the analogous product from the monometallic (R = CH_3) alkynyl.



(VI)

The aforementioned reactions serve to underscore a wide range of behaviors of TCNE toward transition metal organic compounds. Briefly, they are classified as 1,2-addition, 1,4-addition, π-complex formation with "CO insertion", and 1,3-addition with metal migration. In every case, the observed course of reaction may be rationalized in terms of an electrophilic interaction of TCNE with the appropriate electron-rich part of the organometallic molecule. This particular facet, as well as details of our experiments, will be described fully in a later publication.

ACKNOWLEDGMENT

We are grateful to the National Science Foundation for support.

REFERENCES

1 S.R. Su, J.A. Hanna and A. Wojcicki, *J. Organometal. Chem.*, 21 (1970) P21.
2 P.M. Treichel, R.L. Shubkin, K.W. Barnett and D. Reichard, *Inorg. Chem.*, 5 (1966) 1177.
3 W.H. Baddley, *Inorg. Chim. Acta Revs.*, 2 (1968) 7.
4 M. Green, S. Tolson, J. Weaver, D.C. Wood and P. Woodward, *Chem. Commun.*, (1971) 222.
5 J.E. Thomasson, P.W. Robinson, D.A. Ross and A. Wojcicki, *Inorg. Chem.*, 10 (1971) in press.
6 P.W. Robinson and A. Wojcicki, *Chem. Commun.*, (1970) 951.