Journal of Organometallic Chemistry, 159 (1978) C20—C24
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary Communication

MOLECULAR STRUCTURES OF TWO UNEXPECTED METAL COMPLEXES OBTAINED FROM ADDITIONS OF COORDINATED PHOSPHINES TO ACETYLENES

P. M. TREICHEL*, W. K. WONG, and J. C. CALABRESE

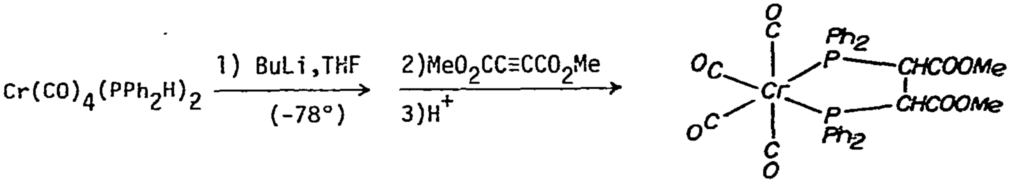
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)

(Received June 1st, 1978)

Summary

The syntheses and structures of two new compounds are reported. The first compound, $[Cr(CO)_4]_2[C_4F_2(PPh_2)_4]$, obtained from $Cr(CO)_4(PPh_2H)_2$ and $CF_3C{\equiv}CCF_3$ in the presence of one equivalent of BuLi has a structure with the ligand 1,2,3,4-tetrakis(diphenylphosphino)-1,4-difluorobutadiene chelating to two $Cr(CO)_4$ groups via the 1,4 and 2,3 phosphine groups. A mechanism for the formation of this compound is suggested which involves sequential deprotonation of a phosphine, nucleophilic attack on the fluorocarbon, and fluoride ion elimination. The second compound, $CrC_{36}H_{28}P_2O_7$, arises from a similar base promoted reaction of $Cr(CO)_4(PPhH_2)_2$ and $PhC{\equiv}CCOOEt$. Here the expected initial product from cyclization of these reactants acts as a nucleophile to attack a second equivalent of the acetylene. The intermediate carbanion from this reaction can undergo a ring closure by displacement of OEt^-, giving the observed product.

Recently [1] we described additions in the presence of equimolar base of the P-H functionality in coordinated secondary phosphines to certain acetylenes having electron withdrawing substituents. These reactions provided a potentially useful route to metal complexes of chelating diphosphines. An illustration is provided in the example below.



In the course of this general study we encountered several anomalous products ~~which defied~~ characterization by traditional methods. Two of these products were finally identified in x-ray crystallographic studies. The structures of these compounds are described in this paper.

The first product was obtained in 18% yield from the acetylene $CF_3C{\equiv}CCF_3$. To an orange solution of cis-$[Cr(CO)_4(PPh_2H)(PPh_2)]^-$, prepared from cis-$Cr(CO)_4(PPh_2H)_2$ and BuLi in THF at -78°, was added $CF_3C{\equiv}CCF_3$. The solution immediately became dark red. Addition of HCl(aq) followed by workup involving alumina chromatography using chloroform as eluting solvent gave (along with starting material) a single product which crystallized from dichloromethane-benzene as a 1:1 benzene solvate (decomp. at 200° without melting, $\nu(CO)$ = 2008s, 1935s, 1893vs, 1873s). A single well shaped crystal was mounted and data obtained using a Syntex $P\bar{1}$ diffractometer. Crystal data: Space group $P\bar{1}$ with two molecules per unit cell of dimensions (Å) $a = 13.442(4)$, $b = 20.151(4)$, $c = 12.573(4)$; $\alpha = 92.65(2)°$, $\beta = 117.04(2)°$, $\gamma = 102.90(2)°$ (Temperature = 25°C); d(calc) = 1.428 g/cm^3, d(found) = 1.425 g/cm^3. A total of 5353 diffraction data $[I > 2\sigma(I)]$ were collected. The structure, solved by direct methods, was refined via anisotropic (all atoms except hydrogens) block diagonal least-squares techniques to $R_1 = 0.051$. The molecular structure is shown in Figure 1. Bond lengths are generally normal in this structure; note that in the seven membered ring there are double bonds between C(9) and C(10) (1.334(7)Å) and between C(11) and C(12) (1.333(7)Å).

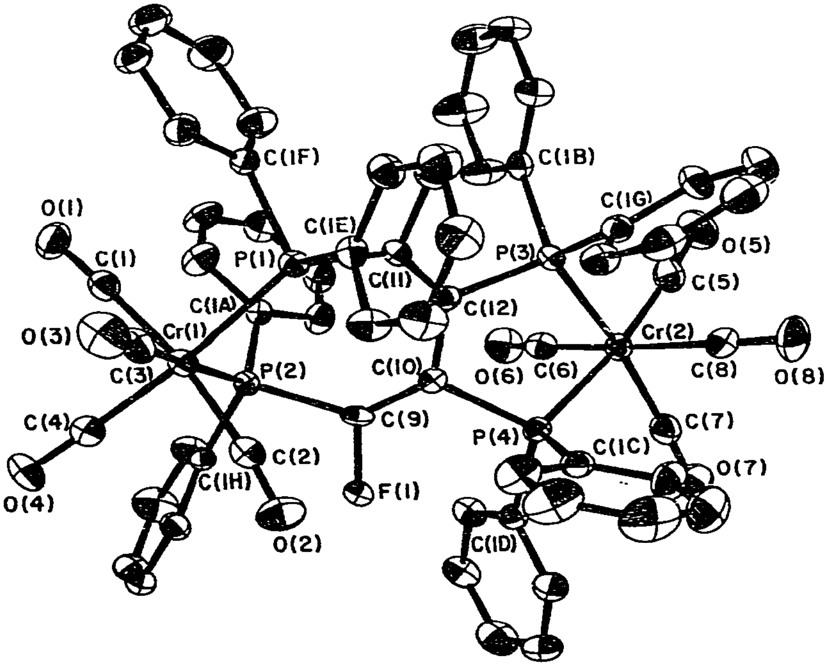
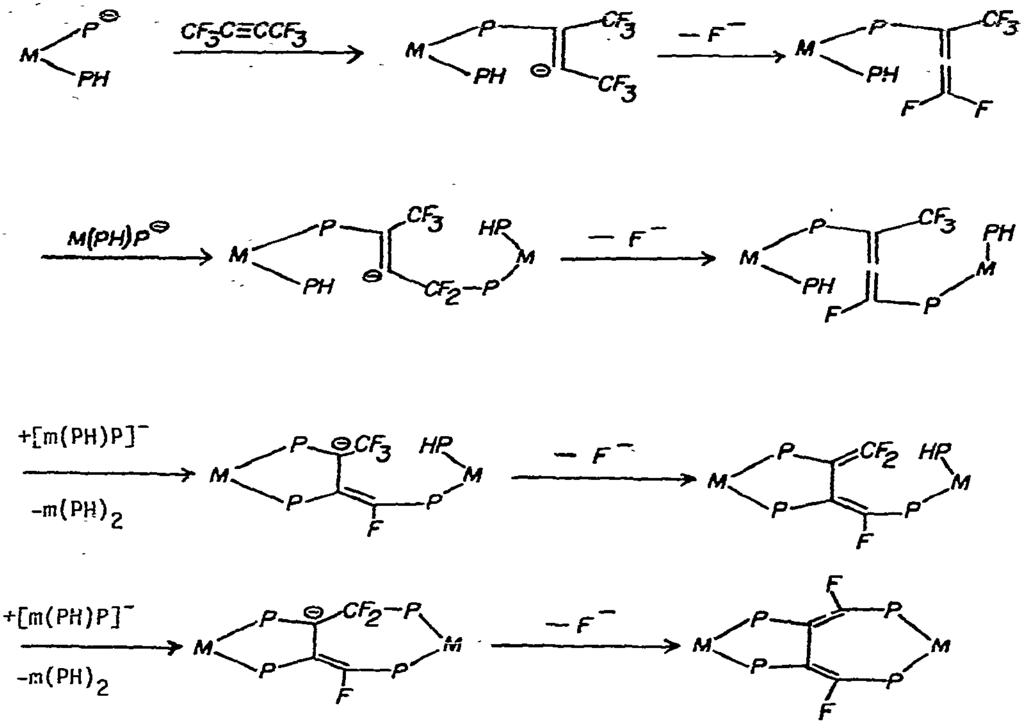


Figure 1. Molecular Structure of $[Cr(CO)_4]_2[C_4F_2(PPh_2)_4]$.

It can be seen that is compound is a 1:2 adduct of acetylene and metal complex lacking four equivalents of HF. A route to this compound can be suggested involving a series of deprotonation steps (involving BuLi) giving carbanion intermediates followed by fluoride loss (Scheme I). The facile fluoride loss is the other distinguishing feature of this reaction. Such a result has been seen in other reactions of nucleophiles with $CF_3C\equiv CCF_3$ [2].

SCHEME I



($m(PH)_2 = Cr(CO)_4(PPh_2H)_2$)

The second unusual compound was obtained in a reaction of $Cr(CO)_4(PPhH_2)_2$ and $PhC\equiv CCOOEt$, carried out essentially in the same fashion. From this reaction a single orange crystalline product was obtained in 26% yield (recrystallized from CH_2Cl_2-pentane, mp 153-155°C, $\nu(CO)$ = 2110s, 1910vs, 1895vs, 1876s; and 1729m, 1687m). Again unable to characterize this compound by standard means, we undertook a crystallographic study; the structure shown in Figure 2 was determined for this compound. Crystal data: Space group C2/c with eight molecules per unit cell of dimensions (Å) a = 29.745(7), b = 11.105(4), c = 21.149(8), and β = 94.12(2)° (Temperature, 25°C); d(calc) = 1.391 g/cm^3, d(found) = 1.398 g/cm^3. Collected were 2679 data for which $[I > 2\sigma(I)]$. The structure was determined by the heavy atom method, all atoms including hydrogens being located. Isotropic and finally anisotropic refinements for all non-hydrogen atoms by block diagonal least

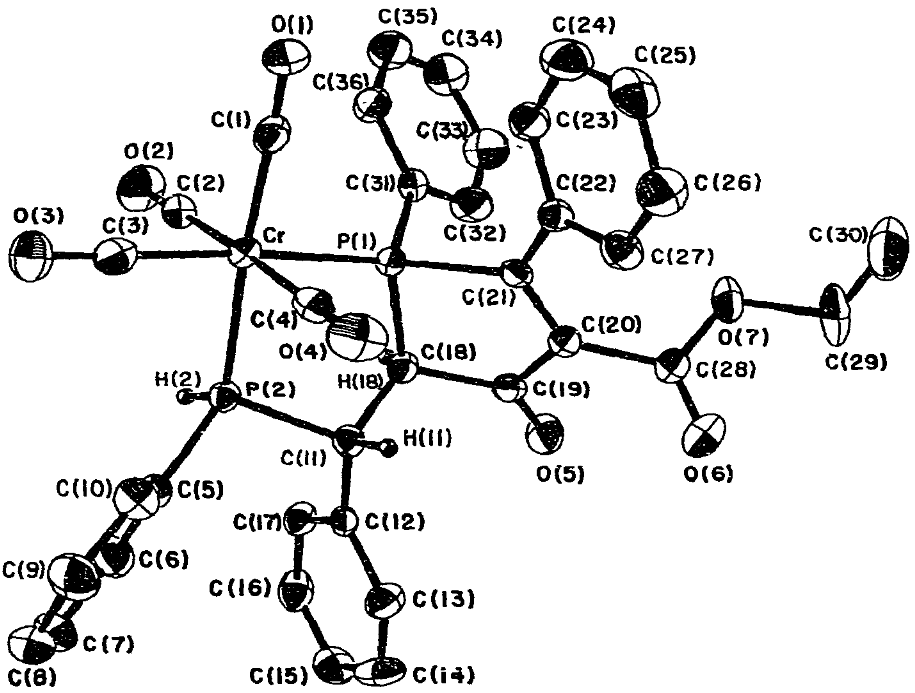


Figure 2. Molecular Structure of $CrC_{36}H_{28}P_2O_7$.

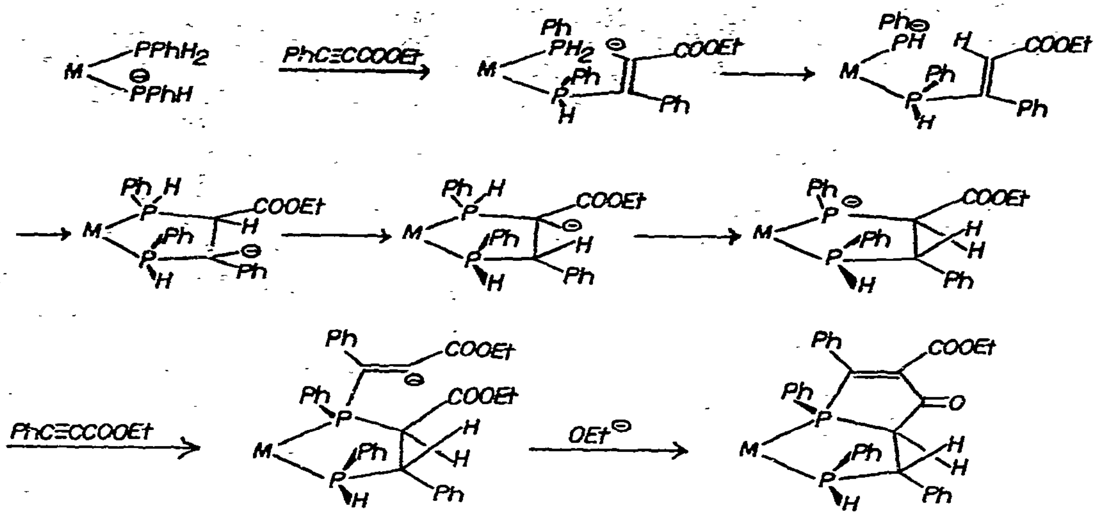
squares yielded the final structural parameters having a final reliability index $R_1 = 0.047$.

Scheme II shows a reasonable route to this complex. The initial Michael-type addition via a stabilized carbanion intermediate generates an initial 1:1 adduct. The trans stereochemistry of the Ph and COOEt groups, preferred on steric grounds, is noted in passing. This anionic intermediate can in turn attack a second molecule of acetylene giving another stabilized carbanion. This, however, is favorably disposed sterically to close on itself by displacement of ethoxide ion from the COOEt group, to give the final product. It is interesting to note this relationship between the two products described here, that both are formed in routes involving an anion elimination. Such reactions, while perhaps limiting the usefulness of these base induced cyclization reactions, are nonetheless mechanistically interesting, and provide a basis for substantial further study.

ACKNOWLEDGEMENT

We acknowledge the University of Wisconsin Graduate School for partial support of this work. The Syntex Diffractometer was purchased by funds made available to the department by the National Science Foundation through a major equipment grant.

SCHEME II



REFERENCES

1. P. M. Treichel and W. K. Wong, J. Organometal. Chem., submitted.
2. R. J. Goodfellow, M. Green, N. Mayne, A. J. Rest, and F. G. A. Stone, J. Chem. Soc. (London) A, (1968) 177.