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PHOTOINITIATED REACTIONS OF $(\eta\text{-}C_5H_5)_2MH_3$ (M = Nb, Ta) WITH $Mn_2(CO)_{10}$: STRUCTURE OF $(\eta\text{-}C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$

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Summary

The photoreaction of $(\eta\text{-}C_5H_5)_2TaH_3$ with $Mn_2(CO)_{10}$ gives, inter alia, $(\eta\text{-}C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$, whose crystal structure reveals an open, bent trimetallic framework. Preliminary mechanistic studies show that this and the analogous niobium reaction proceed via a complex sequence of thermal steps following photoinitiation.

We have previously reported the structure of $[(Cp_2(CO)Nb)_2(\mu\text{-}H)]^+ [Mn(CO)_5]^-$ (I, Cp = $\eta\text{-}C_5H_5$), the ultimate product of the photoreaction of Cp_2NbH_3 with $Mn_2(CO)_{10}$ [1]. A second, non-ionic product II was also isolated but could not be crystallized. We now report the structure of a non-ionic complex obtained from the analogous tantalum reaction, along with preliminary observations on the mechanism of formation of these species.

Near-UV irradiation of a toluene solution of equimolar Cp_2TaH_3 and $Mn_2(CO)_{10}$ at 0°C for 50 min, followed by filtration and storage in the dark, leads to a red solution, which on addition of hexane at 7°C affords red plates whose IR closely resembles that of II. These were too thin for crystallographic study; prolonged cooling of a toluene solution at −78°C afforded large cubic purple crystals (III). A fragment of dimensions $0.4 \times 0.35 \times 0.4$ mm was cut from one of these and examined crystallographically. Crystal data: monoclinic; a 14.872(3), b 10.756(2), c 15.591(3) Å; β 114.04(1)°; space group $P2_1/a$; $Z = 4$. Data were collected from $3.5 < 2\theta < 54.9°$ for a total of 4469 independent reflections used. The Ta atom was located from the Patterson function; subsequent difference Fourier maps revealed the Mn, C, O, bridging H and 8 of the 10 ring H atoms. All but the latter were refined anisotropically to final agreement factors $R = 0.039$ and $R_w = 0.052$.

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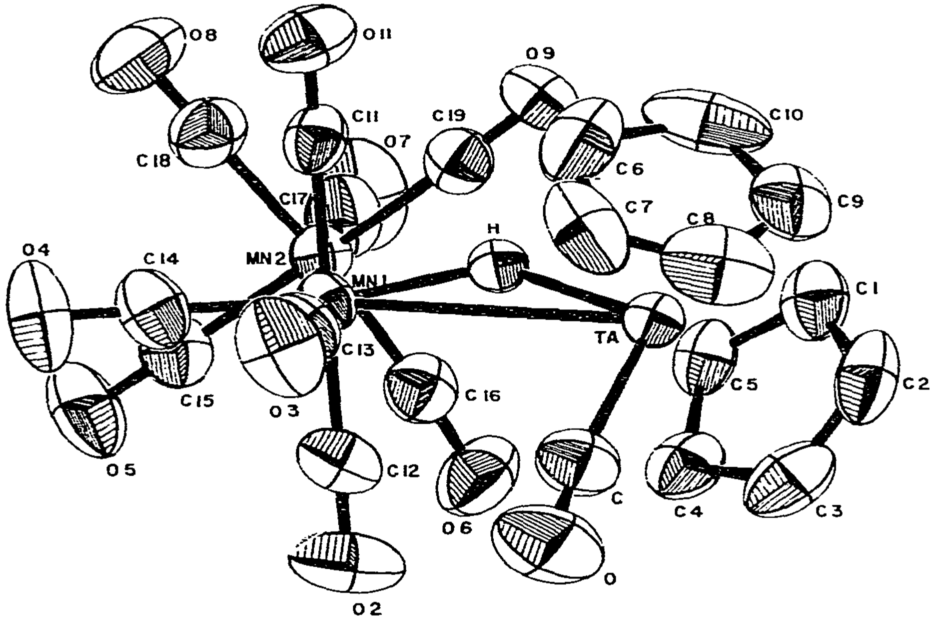

Fig. 1. Structure of compound III.

The structure of III (Fig. 1) identifies the product as the open, bent trimetallic $Cp_2(CO)Ta(\mu-H)Mn(CO)_4Mn(CO)_5$. III may be considered as a member of the general class of complex $Cp_2(CO)M(\mu-H)M'L_n$, wherein the 18-electron group $Cp_2MH(CO)$ (M = Ta here, Nb in all previously determined structures) acts as a 2-electron donor ligand (via a 3-center, 2-electron MHM bond) to the coordinatively unsaturated group $M'L_n$ *. In III, $M'L_n$ is the 34-electron bimetallic fragment $Mn_2(CO)_9$; the "substituent" $Cp_2TaH(CO)$ occupies an equatorial position. III is closely related (and isoelectronic) to known $HRe_2Mn(CO)_{14}$ [6] and $HRe_3(CO)_{14}$ [7] which have the same framework (with M–M–M angles respectively 98.1 and 106.0°; Ta–Mn–Mn = 108.09(3)° in III). The carbonyls on Mn(2) are bent somewhat towards Mn(1) (average C_{ax}–Mn(2)–C_{eq} = 94.6°) and staggered with respect to those on Mn(1), as found in related species [6–8]. The long Ta–Mn(1) distance, 3.441(1) Å, is consistent with the 3-center bonding model [5]; other parameters of interest include: Ta–H, 1.91(5) Å; Mn(1)–H, 1.77(5) Å; Mn(1)–Mn(2), 2.938(1) Å (cf. 2.9038(6) Å in $Mn_2(CO)_{10}$ [8]); and Ta–H–Mn(1), 138.2(3)°. Atoms Ta, H, CO and Mn(1) are all coplanar, as found in all previous structures of this class [1–5].

We have not yet succeeded in crystallizing red niobium compound II or its Ta analog for structural determination. One possibility is that the red and purple compounds are linear and bent isomers respectively; it has been suggested that the relative stability of these two geometries depends upon a balance of steric and electronic effects (e.g., $Mn_3(CO)_{14}^-$ is linear) [7]. It may be noted that all four species have similar IR spectra, while analytical data for II are in reasonable

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* Previous examples include $M'L_n$ = $Fe(CO)_4$ [2]; $CpNb(CO)_3$ [3]; $[Cp_2Nb(CO)]^+$ [1]; and $Ni(CO)_3$ [4] among others [4,5]. A full discussion of this structural class will be presented later [5].

agreement. Found: C, 38.02; H, 2.29. $Cp_2(CO)NbHMn_2(CO)_9$ calcd.: C, 39.11; H, 1.81%. The purple Nb compound, obtained by adding ether to red II, converts rapidly to ionic I on dissolution in polar solvents such as acetone; no ionic analog of I was ever found for Ta.

Based upon Herrmann's findings [3,5], complexes $Cp_2(CO)M(\mu\text{-}H)Mn_2(CO)_9$ are quite reasonable products of these reactions. Surprisingly, though, closer examination shows that they are not in fact primary photoproducts, but rather the result of a photoinitiated reaction wherein some early photoproduct catalyzes a sequence of otherwise slow thermal reactions. This is demonstrated by the fact that irradiation of Cp_2NbH_3 and $Mn_2(CO)_{10}$ (toluene solution, sealed NMR tube, 0°C, 15 min) gives little change in the NMR: besides unreacted Cp_2NbH_3 signals, only a weak peak is observed at δ −7.8 ppm, assigned to $HMn(CO)_5$ [9]. ($HMn(CO)_5$ does not appear to be the catalyst, though: adding it to a dark solution does not reproduce the behavior observed following irradiation.) Maintaining this solution in the dark at 30°C leads to gradual NMR changes: the reaction proceeds via $Cp_2NbH(CO)$ (δ 4.61, −6.4 ppm) and a second, unidentified intermediate (δ 4.55, −14.7 ppm) to product II (δ 4.67, −20.8 ppm). On prolonged standing, I slowly precipitates [1]. (No reaction is observed in an unirradiated NMR tube.) The variety of products obtained * and the complexity of the pathway by which they form is striking, for these at first sight relatively simple reaction systems.

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* Still another Nb–Mn compound in this family, $Cp_2(CO)Nb(\mu\text{-}CO)Mn(CO)_4$, has recently been reported [4].