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Preliminary communication

Synthesis of binuclear metal carbene complexes containing two different transition metals: *cis*-$(CO)_5ReMn(CO)_4C(OCH_3)CH_3$ and *cis*-$(CO)_5ReMn(CO)_4C(OCH_3)C_6H_5$

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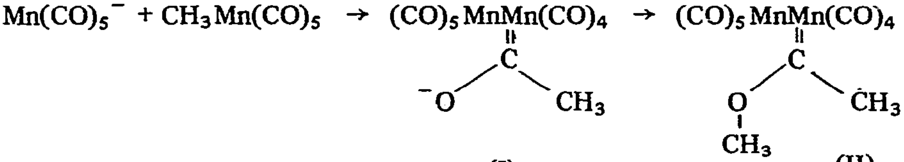
SUMMARY

The reaction of $NaRe(CO)_5$ with $CH_3Mn(CO)_5$ and with $C_6H_5Mn(CO)_5$ followed by alkylation with CH_3OSO_2F gives *cis*-$(CO)_5ReMn(CO)_4C(OCH_3)CH_3$ and *cis*-$(CO)_5ReMn(CO)_4C(OCH_3)C_6H_5$ respectively.

We recently reported[1] the equilibrium reaction of $NaMn(CO)_5$ with $CH_3Mn(CO)_5$, which affords the binuclear acetylmanganese anion I, and the subsequent alkylation of I with $(CH_3)_3O^+\ BF_4^-$ to give the *cis* metal carbene complex II **.



(I) (II)

This new reaction of metal carbonyl anions with alkyl metal carbonyl compounds provides a potentially valuable method of synthesizing binuclear metal carbene complexes***. Here we report the sucessful synthesis of two new crystalline rhenium-manganese carbene complexes using this route. These compounds constitute the first fully characterized binuclear

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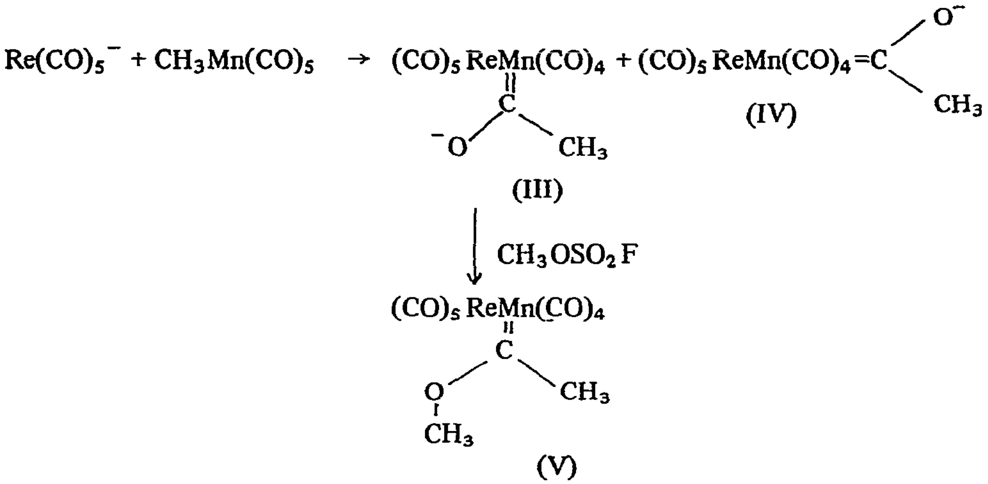
** The acetylmanganese anion I has also been preparaed[2] by reaction of CH_3Li with $Mn_2(CO)_{10}$.

*** A survey of the reaction of metal carbonyl anions with methyl and phenyl metal carbonyls has been carried out[3].

metal carbene complexes containing two different transition metals*.

The reaction of $NaRe(CO)_5$ with $CH_3Mn(CO)_5$ in tetrahydrofuran was readily followed by NMR. The initial NMR spectrum of the reaction mixture was taken 10 minutes after mixing the reagents and showed, in addition to the $CH_3Mn(CO)_5$ resonance at δ −0.1, two new singlets of approximately equal intensity at δ 2.44 and 2.51 which we attribute to the *cis* and *trans* acetyl anions III and IV respectively. The signal at δ 2.51 assigned to IV disappeared within an hour as the signal at δ 2.44 assigned to III increased. After 10 hours, the $CH_3Mn(CO)_5$ resonance had gradually decreased to one-fifth the intensity of resonance assigned to III.



Alkylation of adduct III with methyl fluorosulfonate gave only a single rhenium–manganese binuclear carbon complex, *cis*-$(CO)_5ReMn(CO)_4C(OCH_3)CH_3$, (V) m.p. 107–108° (29% yield) which was purified by preparative layer chromatography (silica gel/pentane) and recrystallization from pentane. (Found: C, 26.34; H, 1.07; Mn, 10.03. $C_{12}H_{16}O_{10}MnRe$ calcd.: C, 26.14; H, 1.10; Mn, 9.97%.)

The NMR spectrum (CS_2) of V consisted of sharp singlets at δ 2.76 and 4.20 as expected for a methylmethoxy carbene complex. The methoxy resonance of V at δ 4.20 is consistent with a *cis* arrangement of the carbene ligand and the rhenium atom; the methoxy resonance of *cis*-$(CO)_5MnMn(CO)_4C(OCH_3)CH_3$ occurs at δ 4.22 while that of *trans*-$(CO)_5MnMn(CO)_4C(OCH_3)CH_3$ occurs at δ 4.62 [5]. The infrared spectrum (heptane) of V had eight bands in the metal carbonyl region at 2093 w, 2038 m, 2017 w, 2002 s, 1994 s, 1979 s, 1960 m, and 1950 m cm^{-1} and established the *cis* relationship of the carbene ligand and rhenium atom. The mass spectrum of V had molecular ions at *m/e* 550 and 552 in a ratio of 1/1.75. ($^{185}Re/^{187}Re$ = 1/1.70) and confirmed the molecular formula of V. The

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* The reaction of $(CO)_5ReMn(CO)_5$ with C_6H_5Li followed by alkylation with $(CH_3)_3O^+BF_4^-$ has been reported[4] to give a yellow oil containing $(CO)_9MnReC(OCH_3)C_6H_5$, $(CO)_9Mn_2C(OCH_3)C_6H_5$ and $(CO)_9Re_2C(OCH_3)C_6H_5$. It was not determined whether the carbene was attached to Mn or Re in the mixed-metal complex.

mass spectrum of V had only very low intensity peaks at *m/e* expected for $MnC(OCH_3)CH_3$ and $ReC(OCH_3)CH_3$ and consequently gave no information concerning whether the methylmethoxycarbene ligand was attached to manganese or to rhenium.

We have assigned the site of attachment of the carbene ligand as being the manganese atom rather than the rhenium atom on the basis of the method of synthesis. Attack of $Re(CO)_5^-$ at the manganese atom of $CH_3Mn(CO)_5$ would be expected to result in methyl migration to a carbonyl ligand attached to manganese to give anion III. It should be pointed out that the attempted reaction of $CH_3Re(CO)_5$ and $NaMn(CO)_5$ did not produce a new acetyl resonance in the NMR spectrum and did not yield a carbene complex upon treatment with CH_3OSO_2F.

The reaction of $C_6H_5Mn(CO)_5$ with $NaRe(CO)_5$ followed by alkylation with CH_3OSO_2F gave a 24% yield of *cis*-$(CO)_5ReMn(CO)_4C(OCH_3)C_6H_5$ [5], m.p. 93–94°; ν_{max}(heptane) 2093 w, 2040 m, 2000 s, 1993 s, 1964 w, and 1951 m cm^{-1}; δ_{TMS}(acetone-d_6) 4.24 (s, 3H, OCH_3), 7.1–7.7 (m, 5H, C_6H_5). (Found: C, 33.07; H, 1.39; Mn, 8.69. $C_{17}H_8O_{10}MnRe$ calcd.: C, 33.29; H, 1.31; Mn, 8.96%.)

REFERENCES

1 C.P. Casey and R.L. Anderson, *J. Amer. Chem. Soc.*, 93 (1971) 3554.
2 E.O. Fischer and E. Offhaus, *Chem. Ber.*, 102 (1969) 2549.
3 C.P. Casey and C.R. Cyr, in preparation.
4 E.O. Fischer, E. Offhaus, J. Müller and D. Nöthe, *Chem. Ber.*, 105 (1972) 3027.
5 C.P. Casey, R.A. Boggs and C.R. Cyr, unpublished results.