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**Preliminary communication**

# NEW CHELATE RING OPENING REACTIONS LEADING TO THE SYNTHESIS OF NOVEL MIXED LIGAND COMPLEXES OF THE OCTAHEDRAL METAL CARBONYLS

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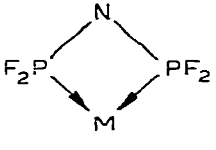
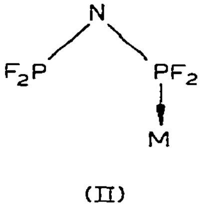
## Summary

Reactions of the four-membered ring chelate $CH_3N(PF_2)_2Cr(CO)_4$ with trivalent phosphorus ligands (L) at 80°C leads to facile opening of the chelate ring to give the mixed ligand complexes *trans*-$CH_3N(PF_2)_2Cr(CO)_4L$ (L = $(C_6H_5)_3P$ or monodentate $C_6H_5N(PF_2)_2$) containing a monodentate $CH_3N(PF_2)_2$ ligand.

Reactions of the ligand $CH_3N(PF_2)_2$ with metal carbonyls [1,2] and metal vapors [3] have been shown to give diverse metal complexes containing biligate monometallic (I) or monoligate monometallic (II) $CH_3N(PF_2)_2$ ligands. This communication reports the first examples of the conversion of a biligate monometallic to a monoligate monometallic $RN(PF_2)_2$ ligand through cleavage of the four-membered chelate ring in I by means of a trivalent phosphorus Lewis base.



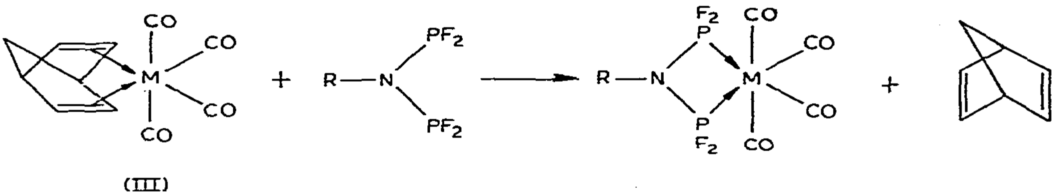
(I)



(II)

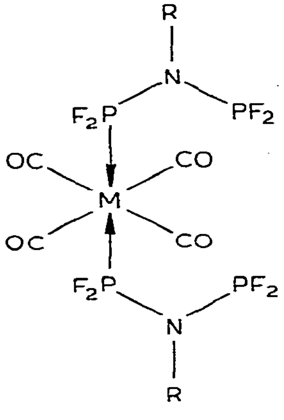
Shortly after his original discovery of the $RN(PF_2)_2$ ligands [4,5] Nixon reported [6] the displacement of norbornadiene in the metal tetracarbonyls III (M = Cr, Mo, and W) by $C_2H_5N(PF_2)_2$ to give the corresponding $C_2H_5N(PF_2)_2$-$M(CO)_4$ chelates (IV: R = $C_2H_5$, M = Cr, Mo, and W) according to reaction 1.

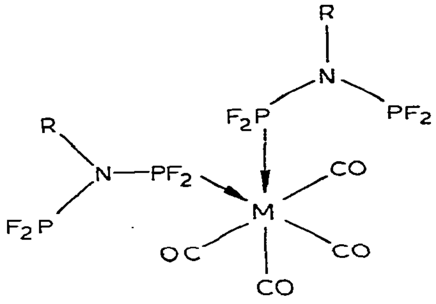
We have used analogous reactions to prepare the corresponding $CH_3N(PF_2)_2$-$M(CO)_4$ (IV: R = $CH_3$, M = Cr, Mo, and W) and $C_6H_5N(PF_2)_2M(CO)_4$ (IV: R =


(III)

(IV)

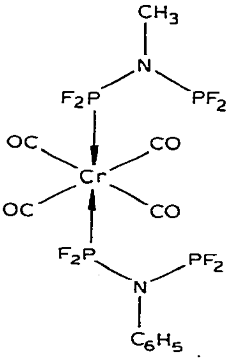
$C_6H_5$, M = Cr, Mo, and W) derivatives. Furthermore, we have found that reactions of the norbornadienemetal tetracarbonyl complexes III with excess $RN(PF_2)_2$ ligand (R = $CH_3$ and $C_6H_5$) in boiling hexane also lead to the replacement of the coordinated norbornadiene by two $RN(PF_2)_2$ ligands*. The chromium complexes $[RN(PF_2)_2]_2Cr(CO)_4$ (R = $CH_3$ and $C_6H_5$) prepared by this reaction exhibit a single strong infrared $\nu$(CO) frequency at 1958 (R = $CH_3$) and 1965 (R = $C_6H_5$) $cm^{-1}$ and two strong Raman $\nu$(CO) frequencies at 2065 and 2000 $cm^{-1}$ (R = $CH_3$) and 2065 and 2000 $cm^{-1}$ (R = $C_6H_5$) indicating formulation as the *trans* isomers Vt (R = $CH_3$ and $C_6H_5$). However, the corresponding molybdenum and tungsten complexes $[RN(PF_2)_2]_2M(CO)_4$ (M = Mo and W) exhibit four infrared $\nu$(CO) frequencies (e.g. 2062m, 2000m, 1986s, and 1977vs in hexane for $[CH_3N(PF_2)_2]_2Mo(CO)_4$) indicating formulation as the *cis* isomers Vc (M = Mo and W).


(Vt)

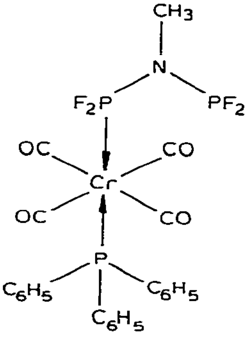

(Vc)

These observations raise the question as to whether the biligate monometallic complexes $RN(PF_2)_2M(CO)_4$ (IV) are intermediates in the formation of the monoligate monometallic complexes $[RN(PF_2)_2]_2M(CO)_4$ (Vt or Vc) from $C_7H_8M(CO)_4$ (III) and $RN(PF_2)_2$ or whether $RN(PF_2)_2M(CO)_4$ (IV) and $[RN(PF_2)_2]_2M(CO)_4$ (Vt or Vc) are formed by independent reaction pathways. In this connection the reaction of $C_6H_5N(PF_2)_2Cr(CO)_4$ (IV: R = $C_6H_5$, M = Cr) with excess $C_6H_5N(PF_2)_2$ in a 1/4 mol ratio in boiling hexane for 48 h was found to result in opening of the four-membered chelate ring to give a 55% yield of *trans*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_4$ (Vt: R = $C_6H_5$, M = Cr), m.p. 120—121°C. This result clearly suggests that the $RN(PF_2)_2M(CO)_4$ derivatives IV are stable intermediates in the formation of $[RN(PF_2)_2]_2M(CO)_4$ derivatives (Vt or Vc) from $C_7H_8M(CO)_4$ (III) and excess $RN(PF_2)_2$.

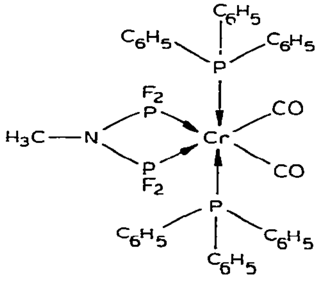
Analogous four-membered chelate ring opening reactions have been used to prepare "mixed ligand" chromium carbonyl complexes of the type *trans*-$RN(PF_2)_2$-$Cr(CO)_4L$ which are among the few known examples of *trans*-$LL'M(CO)_4$ derivatives. Thus reaction of $CH_3N(PF_2)_2Cr(CO)_4$ (IV: R = $CH_3$, M = Cr) with excess $C_6H_5N(PF_2)_2$ in a 1/4 mol ratio in boiling hexane for 48 h gives a 52% yield of the colorless volatile (sublimes at 55°C/0.001 mmHg) mixed ligand complex *trans*-$[CH_3N(PF_2)_2][C_6H_5N(PF_2)_2]Cr(CO)_4$ (VI), m.p. 67—68°C, $\nu$(CO) 1969s $cm^{-1}$; proton NMR in $CDCl_3$: $C_6H_5$ $\delta$ 7.43 and 7.28 ppm; $CH_3$ $\delta$ 2.96 ppm (doublet, $J$ 6 Hz). This product is the first known metal complex containing two different $RN(PF_2)_2$ ligands. Similarly a reaction between equimolar quantities of $CH_3N(PF_2)_2Cr(CO)_4$ and triphenylphosphine in boiling benzene for 24 h gives a 21% yield of the complex *trans*-$CH_3N(PF_2)_2Cr(CO)_4P(C_6H_5)_3$ (VII), m.p. 101—102°C; infrared $\nu$(CO) 1933s $cm^{-1}$; proton NMR in $CDCl_3$: $C_6H_5$ $\delta$ 7.43 ppm; $CH_3$ $\delta$ 2.95 ppm (doublet, $J$ 7 Hz). A minor less soluble byproduct ($\sim$4% yield) from this $CH_3N(PF_2)_2Cr(CO)_4/(C_6H_5)_3P$ reaction is the carbonyl substitution product $CH_3N(PF_2)_2Cr(CO)_2[P(C_6H_5)_3]_2$, m.p. 205°C; formulated as VIII on the basis of its infrared spectrum ($\nu$(CO): 1932s and 1890s $cm^{-1}$ ( indicating relative *cis*-positions of the two carbonyl groups and a triplet methyl resonance in its proton NMR spectrum ($CH_3$ $\delta$ 3.25 ppm, $J$ 12 Hz) indicating a biligate monometallic $CH_3N(PF_2)_2$ ligand [2]. The net result of the reaction between $CH_3N(PF_2)_2Cr(CO)_4$ and triphenylphosphine thus can be either chelate ring opening to produce VII or carbonyl substitution to produce VIII.



(VI)



(VII)



(VIII)

The preliminary observations summarized in this Communication suggest that reactions of $RN(PF_2)_2M(CO)_4$ derivatives (IV: M = Cr, Mo, and W) with Lewis bases can lead to interesting new types of mixed ligand octahedral metal carbonyl derivatives including representatives of the rare compound type *trans*-$LL'M(CO)_4$.

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