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Two-, Four-, Five- and Six-coordinated Metal Complexes Containing the Organometallic Chelate $C_5H_5M[P(OMe)_2O]_2^-$, M = Ni and Pd

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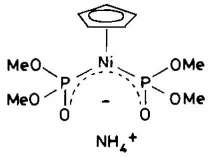
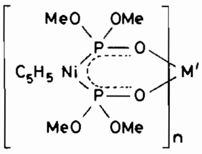
In the course of our investigations on ring ligand displacement reactions of dicyclopentadienyl metal complexes [1] we have also studied the reaction of nickelocene with the secondary phosphite $HP(O)(OMe)_2$ and isolated the $NH_4^{\oplus}$ salt of the nickelabis(phosphonate) anion, (I) [2]. Subsequent reaction of (I) with $ZnCl_2$ or $CoCl_2$ gives the complexes $\{C_5H_5Ni[P(OMe)_2O]_2\}_2Zn$ and $\{C_5H_5Ni[P(OMe)_2O]_2\}_2Co$ which have a spiro center at the central metal atom [2]. Our continuing interest in this subject has now led to an alternative method for obtaining mono-, bis- and tris-chelate complexes of the general type (II). Furthermore, analogous complexes possessing palladium instead of nickel in the chelating system have also become accessible.



(I)



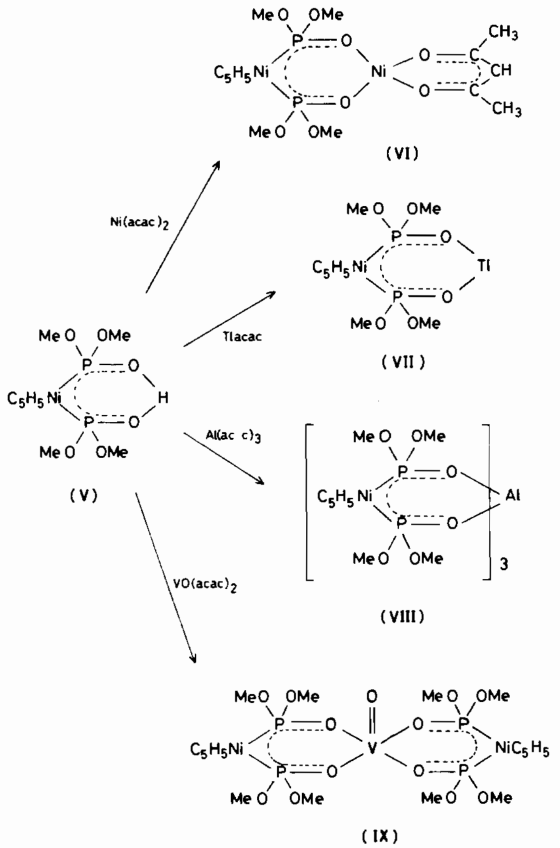
(II)

$\{C_5H_5Ni[P(OMe)_2O]_2\}NH_4$ (I) reacts with $[Ni(NH_3)_6]Cl_2$ to form the octahedral bisammine complex (III) which on heating to 130 °C under vacuum eliminates two NH_3 molecules to give (IV). Attempts to obtain (IV) by starting with the hydrogen bridge complex (V) – which is the product of the reaction of $Ni(C_5H_5)_2$ and $HP(O)(OMe)_2$ – and $Ni(acac)_2$ failed but led to the new complex (VI) in which the "classical" chelating ligand $acac^-$ and the organometallic counterpart $C_5H_5Ni[P(OMe)_2O]_2^-$ are linked to the same central metal. The magnetic moment of (VI), μ = 3.04 B.M. (determined by the n.m.r. method [3]) points to a tetrahedral coordination of Ni(II):

$$\text{(I)} \xrightarrow{[Ni(NH_3)_6]Cl_2} \underset{\text{(III)}}{\{C_5H_5Ni[P(OMe)_2O]_2\}_2Ni(NH_3)_2}$$

$$\xrightarrow[-2NH_3]{\Delta} \underset{\text{(IV)}}{\{C_5H_5Ni[P(OMe)_2O]_2\}_2Ni}$$

The smooth reaction of (V) and $Ni(acac)_2$ prompted us to study also the reactivity of other acetylacetonate complexes towards (V). The results so far obtained are summarized in Scheme 1:



Scheme 1.

The Tl and Al containing complexes (VII) and (VIII) are diamagnetic whereas the vanadyl complex is paramagnetic with a magnetic moment of μ = 2.03 B.M. The ^1H n.m.r. spectra of (VII) and (VIII) show only two signals for the cyclopentadienyl and the methoxy protons [VII: δ (ppm) = 5.28, s, C_5H_5; 3.45, vt, OCH_3; in benzene; VIII: δ = 5.35, bs, C_5H_5; 3.65, vt, OCH_3, in $CDCl_3$] thus proving the symmetric arrangement of the chelate rings.

The reaction of $C_5H_5Pd(2\text{-}MeC_3H_4)$ with $HP(O)(OMe)_2$ (molar ratio 1:2) in benzene yields (X) which is the palladium analogue of (V). The yellow crystals are thermally not very stable and slowly decompose in solution (*e.g.*, in benzene) even at room temperature. (X) reacts with Tlacac, $Al(acac)_3$ and $VO(acac)_2$ to give the corresponding chelate com-

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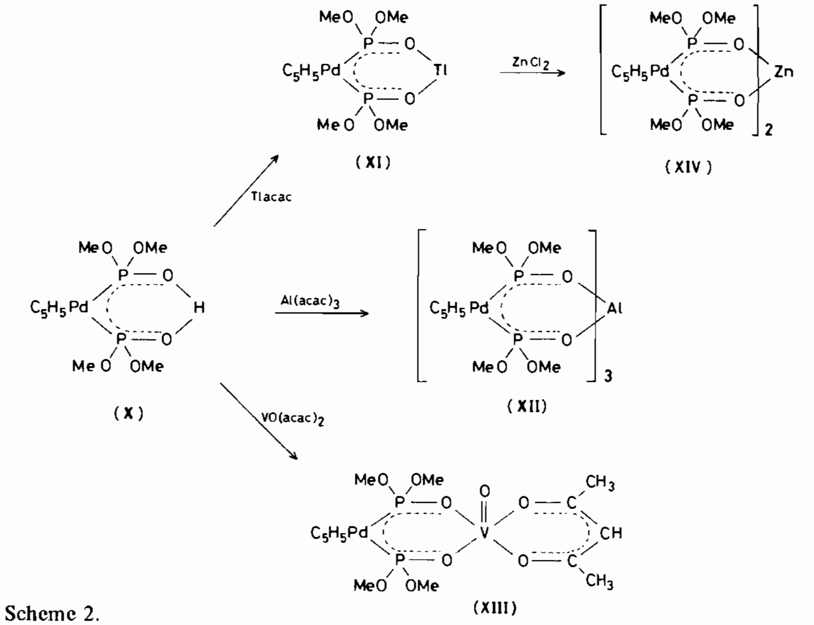


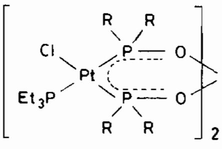
Scheme 2.

pounds (XI)–(XIII) (Scheme 2). In contrast to the reaction of (V) and $VO(acac)_2$ which gives (IX), in the reaction of (X) and $VO(acac)_2$ only one acetylacetonate ligand is displaced by the organometallic chelate. The ^1H n.m.r. spectra of (XI) and (XII) in benzene again show only two signals at $\delta = 5.70$, t, $J_{PH} = 3.1$ Hz, C_5H_5; 3.40 vt, OCH_3, and at $\delta = 5.72$, t, $J_{PH} = 3.1$ Hz, C_5H_5; 3.50, vt, OCH_3, respectively.

The utility of the Tl complex (XI) for further synthetic purposes is demonstrated by the reaction with $ZnCl_2$ in CH_2Cl_2 to form (XIV) [^1H n.m.r.: $\delta = 5.68$; t, $J_{PH} = 3.2$ Hz, C_5H_5; 3.48, vt, OCH_3; in benzene]. Attempts to obtain (XIV) and other complexes of the general type $\{C_5H_5Pd[P(OMe)_2O]_2\}_nM'$ by the same route which was used for the nickel analogues failed since the reaction of (X) with NH_3 leads to rapid decomposition by formation of palladium metal.

The new chelate complexes which are summarised in the schemes were characterised both by elemental analysis and by mass spectra. Even in those cases [*e.g.*, for (XII) and (XIV)] where the molecular weight is rather high the molecular ion is seen with reasonable intensity. The fragmentation of the nickel containing complexes involves first loss of the OMe, $P(O)(OMe)_2$ and $HP(O)(OMe)_2$ groups and then the C_5H_5–Ni bonds are cleaved. In the mass spectra of the palladium analogues the fragmentation may involve either loss of OMe, $P(O)(OMe)_2$ and $HP(O)(OMe)_2$ or of the C_5H_5 group as the first step. It seems to be generally valid that the cyclopentadienyl–nickel bond is more stable than the cyclopentadienyl–palladium bond in complexes of this type [4].

The complexes described here, $\{C_5H_5M[P(OMe)_2O]_2\}_nM'$ (M = Ni, Pd; M' = Tl, Al, VO, Zn), extend the series of complexes (XVI) (M' = VO; R = Ph [5], and M' = Co, Cu, UO_2; R = Ph, OMe [6]) recently synthesised and show that cyclopentadienyl–metal moieties are suitable as components in chelating ring systems.



(XVI)

Acknowledgments

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