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Preliminary communication

OXIDATIVE ADDITION OF α-KETOIMIDOYL CHLORIDES TO PALLADIUM(0) AND PLATINUM(0) COMPLEXES

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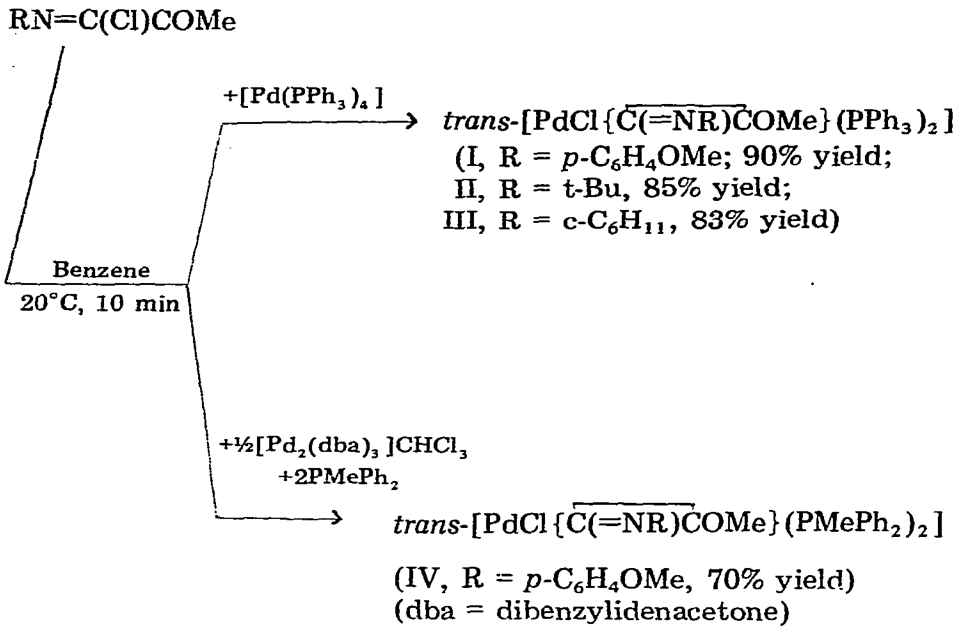
Summary

The reaction of α-ketoimidoyl chlorides with palladium(0) and platinum(0) derivatives yields *trans*-$[MCl\{\overline{C(=NR)C}OMe\}(PMe_nPh_{3-n})_2]$ (M = Pd; R = p-C_6H_4OMe, c-C_6H_{11}, t-Bu; n = 0, 1; M = Pt; R = p-C_6H_4OMe; n = 1) and *cis*-$[PtCl\{C(=N$-p-$C_6H_4OMe)COMe)COMe\}(PPh_3)_2]$, which have been characterized by IR, ^1H and ^{31}P NMR spectra and by condensation with $MeNH_2$.

The reactions of imidoyl chlorides with transition metal substrates have been widely used to prepare complexes containing the imidoyl ligands [1—5]. In previous papers we reported that the acid-catalyzed hydrolysis of 1,4-diaza-3-methylbutadiene-2-yl-palladium(II) compounds yields the corresponding α-ketoimidoyl derivatives [6], from which new 1,4-diazadienyl groups with asymmetrically substituted imino nitrogen atoms can be obtained by condensation with primary amines [7]. We have now found a more convenient route to these compounds based on the oxidative addition of α-ketoimidoyl chlorides [8] to palladium(0) complexes (eq. 1).

Attempts to extend reaction 1 to other d^{10} metal complexes, such as $[M(CH_2{=}CH_2)(PPh_3)_2]$ (M = Ni, Pt), $[PtL_4]$ (L = PPh_3, $PMePh_2$), $[RhCl(PPh_3)_3]$, $[M'Cl(CO)(PPh_3)_2]$ (M' = Rh, Ir), have been successful only for platinum(0) derivatives and for R = p-C_6H_4OMe (eq. 2).



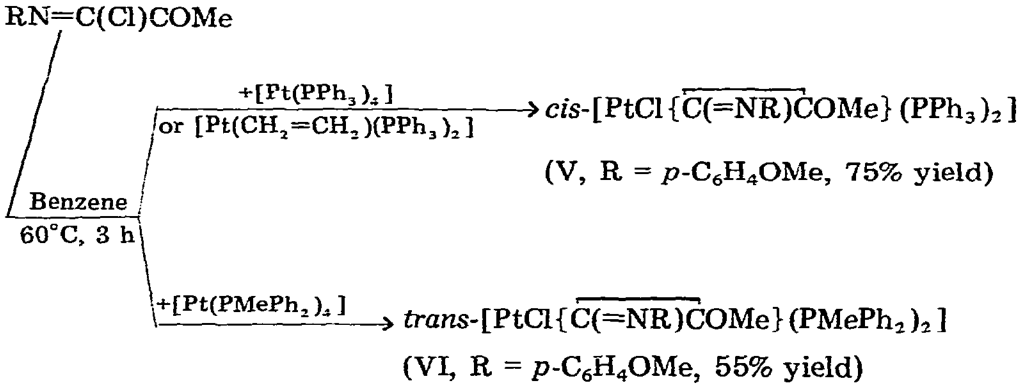
$$\mathrm{RN{=}C(Cl)COMe}\xrightarrow[\text{Benzene, 20°C, 10 min}]{+[\mathrm{Pd(PPh_3)_4}]} trans\text{-}[\mathrm{PdCl\{\overline{C({=}NR)C}OMe\}(PPh_3)_2}]$$

$(\mathrm{I},\ \mathrm{R} = p\text{-}\mathrm{C_6H_4OMe}$; 90% yield; $\mathrm{II},\ \mathrm{R} = \text{t-Bu}$, 85% yield; $\mathrm{III},\ \mathrm{R} = c\text{-}\mathrm{C_6H_{11}}$, 83% yield)

$$\mathrm{RN{=}C(Cl)COMe}\xrightarrow[\text{Benzene, 20°C, 10 min}]{+\tfrac{1}{2}[\mathrm{Pd_2(dba)_3}]\mathrm{CHCl_3}\ +2\mathrm{PMePh_2}} trans\text{-}[\mathrm{PdCl\{\overline{C({=}NR)C}OMe\}(PMePh_2)_2}]$$

$(\mathrm{IV},\ \mathrm{R} = p\text{-}\mathrm{C_6H_4OMe}$, 70% yield)
(dba = dibenzylidenacetone)

(1)



$$\mathrm{RN{=}C(Cl)COMe}\xrightarrow[\text{Benzene, 60°C, 3 h}]{+[\mathrm{Pt(PPh_3)_4}]\ \text{or}\ [\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}]} cis\text{-}[\mathrm{PtCl\{\overline{C({=}NR)C}OMe\}(PPh_3)_2}]$$

$(\mathrm{V},\ \mathrm{R} = p\text{-}\mathrm{C_6H_4OMe}$, 75% yield)

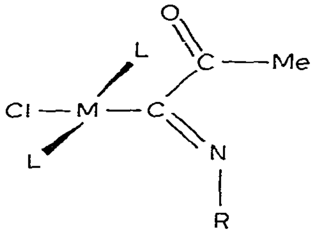
$$\mathrm{RN{=}C(Cl)COMe}\xrightarrow[\text{Benzene, 60°C, 3 h}]{+[\mathrm{Pt(PMePh_2)_4}]} trans\text{-}[\mathrm{PtCl\{\overline{C({=}NR)C}OMe\}(PMePh_2)_2}]$$

$(\mathrm{VI},\ \mathrm{R} = p\text{-}\mathrm{C_6H_4OMe}$, 55% yield)

(2)

All the complexes I—VI give satisfactory elemental analyses and are monomeric in 1,2-dichloroethane. The ν(C=O) and ν(C=N) bands of the α-ketoimidoyl chlorides (1728—1723 and 1666—1638 cm^{-1} in benzene solution, respectively are shifted to lower frequencies [ca. 40—50 cm^{-1} for ν(C=O) and ca. 70—90 cm^{-1} for ν(C=N)] in the corresponding metal derivatives I—VI.

The ^{31}P NMR signals appear as a singlet for I—III ($\mathrm{CD_2Cl_2}$ solution: I 40.06, II 37.38, III 41.75 ppm down-field from external $\mathrm{PEt_3}$) and as a singlet flanked by ^{195}Pt satellites for VI [24.06 ppm, ^1J(Pt—P) = 3037 Hz]. In the ^{1}H NMR spectra ($\mathrm{CD_2Cl_2}$ solution) the δ(PMe) signals occur as a triplet at 1.89 ppm for IV [^2J(P—H) + ^4J(P′—H) = 6.8 Hz] and as a triplet with ^{195}Pt satellites at 2.02 ppm for VI [^2J(P—H) + ^4J(P′—H) = 7.0 Hz, ^3J(Pt—H) = 31.4 Hz]. These results indicate a *trans* configuration for I—IV and VI and the presence of a plane of symmetry perpendicular to the coordination plane across the Cl—M—$C_{imidoyl}$ unit. Although a time-averaged plane of symmetry might be generated by a fast rotation (on the NMR time scale) around the M—$C_{imidoyl}$ bond, steric and electronic factors suggest a configuration of type A, with a planar O=C—C=N conjugated unit, analogous to the structure of the related compound *trans*-[PdCl{$\overline{\mathrm{C(=NR)C}}$(Me)=NR}$(PPh_3)_2$] (R = *p*-$C_6H_4OMe$) [9]:



(A , M = Pd , L = PPh_3 ,$PMePh_2$;
M = Pt , L = $PMePh_2$)

This configuration would also account for the down-field shift of the *ortho* protons of the N*p*-C_6H_4OMe group, resulting from the deshielding effect of the metal atom in close proximity (I δ = 7.60—7.75 ppm; IV 7.65—7.80 ppm; VI 7.70—7.85 ppm) and for the high-field shift of the methyl protons of the COMe group, due to the shielding effect of the phenyl ring current of two mutually *trans* PPh_3 ligands (I δ = 1.34 ppm; II 1.23 ppm; III 1.31 ppm) [9].

When a PPh_3-platinum(0) substrate is used in reaction 2, a *cis* product V is obtained, as shown by its ^{31}P NMR spectrum in CD_2Cl_2 (δ = 32.09 ppm, ^1J(Pt—P) = 4504 Hz, for P *trans* to chlorine; δ = 37.60 ppm, ^1J(Pt—P) = 1729 Hz, for P *trans* to carbon, ^2J(P—P′) = 17.1 Hz). The different geometry of complexes V and VI is also reflected in the different ν(Pt—Cl) values, 295 and 270 cm^{-1}, respectively, resulting from the higher *trans*-influence of the α-ketoimidoyl group compared to PPh_3. Accordingly, in the *trans* complexes I—IV in the ν(Pd—Cl) band was found in the low frequency range 270—250 cm^{-1}.

The compounds I and III undergo condensation reaction at the carbonyl group by $MeNH_2$ to give the 1,4-diazadienyl derivatives *trans*-[PdCl{$\overline{\mathrm{C(=NR)C}}$(Me)=NMe}$(PPh_3)_2$] (R = *p*-$C_6H_4OMe$, *c*-$C_6H_{11}$) [7]. We are now studying this condensation reaction with the platinum complexes V and VI, and the reaction of α-ketoimidoyl chlorides with some metal carbonyl anions.

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