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Preliminary communication

THE REACTIVITY OF METHYLNICKEL, -PALLADIUM AND -PLATINUM COMPOUNDS TOWARDS ALKENES AND ALKYNES

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Summary

The reactivity of alkyl-transition metals towards alkenes and alkynes falls in the sequence $Et_2Ni(bipy) > Et_2Pt(bipy) > Me_2Pt(bipy) > MePtCl(bipy) > MePdCl(bipy)$, which is also the order of decreasing energy of the filled metal *d*-orbitals.

It has been suggested that the reactivity of alkyl-transition metals towards alkenes and alkynes depends on the energy of the filled *d*-orbitals on the metal [1—3]. We have attempted to confirm this by studying reactions of alkenes and alkynes with alkyl derivatives of nickel, palladium and platinum stabilised by the ligand 2,2′-bipyridyl (bipy). The compounds are particularly useful since their UV spectra contain MLCT bands arising from transitions of electrons from filled *d*-orbitals on the metal to π^* orbitals of coordinated 2,2′-bipyridyl. If the energy of these π^* orbitals remains constant an estimate of the energy of the filled *d*-orbitals on the metal can be obtained. The energies of the *d*-orbitals, estimated from the energy of the first MLCT band in acetone solution (given in parentheses), follows the series $Et_2Ni(bipy)$ (15.0×10^3 cm^{-1}) [1] > $Et_2Pt(bipy)$ (21.2×10^3 cm^{-1}) > $Me_2Pt(bipy)$ (21.7×10^3 cm^{-1}) > MePtCl(bipy) (23.8×10^3 cm^{-1}) > MePdCl(bipy) (30.2×10^3 cm^{-1}) and this series also reflects the reactivity of these compounds towards alkenes and alkynes. Direct quantitative comparisons are difficult due to the wide range of reactivities, but the reactivity series can be built up by comparing reactivity of neighbouring pairs. Thus the second-order rate constants for reactions with methyl acrylate at 35°C are 0.15 l mol^{-1} min^{-1} for $Et_2Ni(bipy)$ [1] and 3.0×10^{-3} l mol^{-1} min^{-1} for $Et_2Pt(bipy)$; $Me_2Pt(bipy)$ reacts too slowly with this alkene for convenient measurement of rate constants while MePtCl(bipy) and MePdCl(bipy) fail to react. $Me_2Pt(bipy)$ reacts with acrylonitrile and fumaronitrile to give 1/1 adducts but again MePtCl(bipy) and MePdCl(bipy) do not react. MePtCl(bipy) reacts

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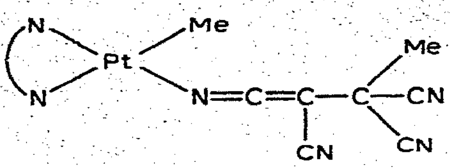
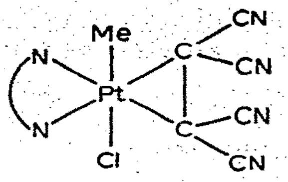


(I)



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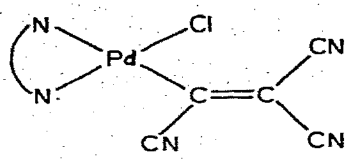

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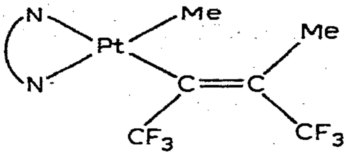

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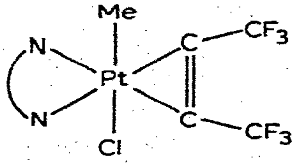

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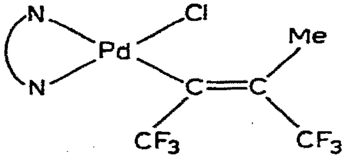

(VI)

= 2,2′-bipyridyl

with hexafluoro-2-butyne very rapidly at room temperature but reaction of this acetylene with MePdCl(bipy) takes several hours to reach completion under similar conditions. The greater reactivity of methylplatinum over methylpalladium compounds towards alkenes has been established previously [2]. This dependence of reactivity on the energy of the filled *d*-orbitals on the metal is easily understood if the initial coordination of the alkene to the metal involves primarily donation of electron density from metal *d*-orbitals into π^* orbitals of the alkene.

The nature of the final products obtained depends on the particular metal complex. For example, tetracyanoethylene (TCNE) reacts with Et_2Ni(bipy) or Me_2Ni(bipy) to give Ni(TCNE) (bipy) [1], with Me_2Pt(bipy) to give (I), with MePtCl(bipy) to give (II) and with MePdCl(bipy) to give (III). Hexafluoro-2-butyne reacts with Me_2Pt(bipy) to give (IV), with MePtCl(bipy) to give (V) and with MePdCl(bipy) to give (VI)*. This reaction is the first example of the insertion of an olefin or acetylene into a methylpalladium bond.

Thus, although the overall reactivity of these alkyl-transition metals

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*Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

towards alkenes and alkynes depends on the energy of the filled metal *d*-orbitals, the factors determining the nature of the final products are more complex and may include factors such as the strength of the initial metal—alkyl bond.

References

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