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Preliminary communication

OLEFIN ISOMERISATION BY GROUP VIA METALS

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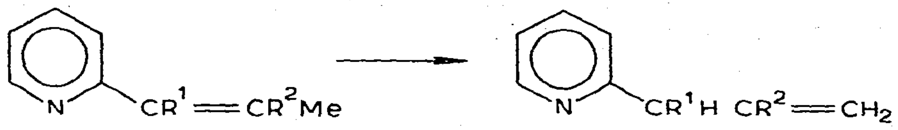
Summary

2-($MeR^1C{=}CR^2$)- and 2-($CH_2{=}CR^1CH_2CH_2$)-pyridine (R^1,R^2 = H or Me) undergo 1,2-double-bond shifts and 2-($CH_2{=}CHCH_2CH_2CH_2$)-pyridine undergoes a 1,3-double-bond shift on displacement of norbornadiene from [$M(CO)_4$norb] (M = Cr, Mo or W) to give complexes of the type [$M(CO)_4LL'$] (LL' = 2-(allyl)- or 2-(substituted allyl)-pyridine), which do not exhibit conformational isomerism involving the plane of the coordinated olefin.

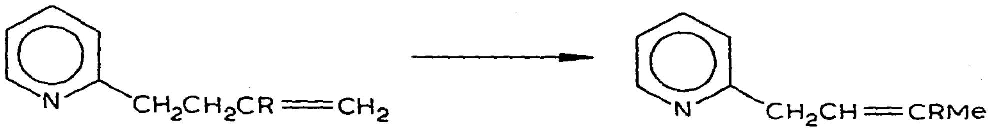
Nyholm et al. [1,2] have shown that (*o*-allylphenyl)diphenylphosphine (AP) undergoes isomerisation on displacement of norbornadiene from [$M(CO)_4$norb] (M = Cr, Mo or W). An X-ray structural determination of the resulting molybdenum complex, [$Mo(CO)_4PP$] (PP = *o*-(1-propenyl)phenyldiphenylphosphine) shows PP to have a *cis*-configuration and to be coordinated to molybdenum in a bidentate manner with the coordinated olefin in the same plane as the molybdenum and phosphorus atoms [3]. Recently similar complexes have been prepared and in the case of [$M(CO)_4LL'$] (M = Mo or W; LL' = (*o*-vinylphenyl)dimethylarsine, (*o*-vinylphenyl)diphenyl-phosphine and -arsine) IR spectroscopy suggests the presence of two conformers; one having the coordinated olefin in the same plane as the metal and the donor atom and the other having the coordinated olefin at right angles to this plane [4].

Attempts to produce Group VI metal tetracarbonyl complexes containing the non-conjugated ligand, 1,5-cyclooctadiene, by isomerisation of 1,3- or 1,4-cyclooctadienes were not very successful [5] and it seemed possible that the successful isomerisation of AP to PP might be due to the olefinic group becoming conjugated to the aromatic ring and the ability of PP to bond to the metal in a bidentate manner to form a stable five-membered ring. It was therefore of interest to examine the versatility of this isomerisation with other less sterically constrained, potentially bidentate, monoolefin ligands containing a donor atom and to examine the resulting products for conformational isomerism.

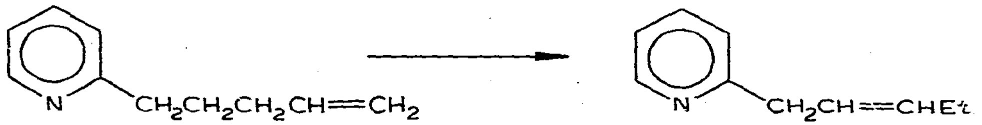
We find that the reaction of $[M(CO)_4norb]$ (M = Cr, Mo or W) with 2-(alkenyl)-pyridines gives products of the type $[M(CO)_4LL']$[*] where LL' is the ligand which has resulted from the following isomerisations:



$R^1 = R^2 = H$ (2-MVPy) → (APy)
$R^1 = H, R^2 = Me$ (2,2-DMVPy) → (2-MAPy)
$R^1 = Me, R^2 = H$ (1,2-DMVPy) → (1-MAPy)



R = H (BPy) → (3-MAPy)
R = Me (3-MBPy) → (3,3-DMAPy)



(3-EAPy)

The ^1H NMR spectra of the above complexes have been completely assigned and are entirely consistent with the above isomerisations having occurred. Additionally we have prepared $[M(CO)_4LL']$ (LL' = 1-MAPy, M = W; LL' = APy, M = Mo or W) directly from authentic 1-MAPy and APy respectively; the other complexes have not been prepared directly because they contain 2-(substituted allyl)-pyridines which are not otherwise easily prepared. It should be noted that no isomerisation of 2-(5-hexenyl)-pyridine (HPy) occurred on reaction with $[M(CO)_4norb]$ and both reactants could be recovered almost quantitatively. A similar reaction with (3-butenyl)diphenylphosphine (BP) gave $[Mo(CO)_4BP]$ whereas (4-pentenyl)diphenylphosphine (PeP) gave only $[Mo(CO)_4(PeP)_2]$ in which PeP behaves as a monodentate ligand with the olefin uncoordinated.

Thus 2-(alkenyl)-pyridines undergo 1,2-double-bond shifts both inwards and outwards from the pyridine ring and also 1,3-double-bond shifts. In all cases, isomerisation results in the formation of a complex containing a 2-(allyl)- or 2-(substituted allyl)-pyridine, which is coordinated in a bidentate manner to give a stable five-membered ring and this must be the important factor in determining the final position of the double bond in the alkene side-chain.

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[*] All the complexes analysed correctly and gave satisfactory molecular weights. The IR spectra show the characteristic shifts associated with coordination of the olefinic group to the metal.

Since no isomerisation is observed with the less sterically constrained ligands HPy and PeP, this suggests that in order for isomerisation to occur the alkene side-chain must be favourably orientated with respect to the metal and lends support to the previously suggested intramolecular mechanism for the isomerisation of AP to PP by Group VIA metals [6].

TABLE 1

IR BANDS DUE TO ν(CO) AT ROOM TEMPERATURE IN n-HEXANE SOLUTION

Complex	ν(CO)					
[W(CO)$_4$(APy)]	2028	1931	1926	1886		
[W(CO)$_4$(1-MAPy)]	2028	1932	1927	1888		
[W(CO)$_4$(2-MAPy)]	2025	1931	1920	1884		
[W(CO)$_4$(*cis*-3-MAPy)]	2020	1925	1918	1879		
[W(CO)$_4$(3,3-DMAPy)]	2020	1919	1909	1876		
[W(CO)$_4$(*cis*-3-EAPy)]	2025	1925	1920	1882		
[Mo(CO)$_4$BP]	2035	1951	1942	1934	1922	1903

It is to be expected that complexes of the type [M(CO)$_4$LL'] (LL' = unsymmetrical bidentate ligand) will have four ν(CO) bands in both the Raman and IR spectra. This is always found to be the case for the above 2-(alkenyl)-pyridine complexes in the Raman spectrum and in the IR spectrum when it was possible to obtain IR spectra in hexane solution (see Table 1); all the complexes are much more soluble in chloroform, but in this solvent only three ν(CO) bands are observed in the IR spectrum. However, never more than four ν(CO) bands are observed in either the Raman or IR spectra of tetracarbonyl Group VIA metal complexes containing 2-(allyl)- or 2-(substituted allyl)-pyridines, and thus it may safely be concluded that, in these complexes, conformational isomerism involving the plane of coordination of the olefin is not occurring. This is to be contrasted with the IR spectrum of a hexane solution of [Mo(CO)$_4$BP] which shows at least six ν(CO) bands (see Table 1) and thus appears to exhibit conformational isomerism similar to that recently discussed [4].

Acknowledgement

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