Reactions between Trimethylenemethane Metal Complexes and the Carbon–Nitrogen Double Bond: Nickel and Palladium catalysed Synthesis of Pyrrolidines

Michael D. Jones and Raymond D. W. Kemmitt

Inorganic Research Laboratories, Department of Chemistry, The University, Leicester LE1 7RH, U.K.

The d^{10} nickel complex $[\mathrm{Ni}\{\mathrm{P(OEt)_3}\}_4]$ catalyses the cycloaddition of trimethylenemethane to the C=N double bond of an imine to afford a high-yield synthesis of 4-methylenepyrrolidines.

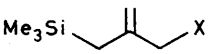
Current interest in metal complexes of trimethylenemethane (tmm)[1] and palladium mediated cycloaddition of tmm to C=C and C=O double bonds[2] prompts us to report the first metal catalysed additions of tmm to the C=N double bond using a readily available nickel(0) complex $[\mathrm{Ni}\{\mathrm{P(OEt)_3}\}_4]$.

We have previously reported that 3-trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene (**1a**), the chloride (**1b**), and the acetate (**1c**) all serve as a new entry into η^4-tmm metal complexes.[1,3,4] Notably reactions of the mesylate (**1a**) with d^8 metal centres afforded high yields of the first η^4-tmm complexes of ruthenium, osmium, rhodium, and iridium, *e.g.* equation (1). By contrast reactions of the mesylate (**1a**) with d^{10} metal complexes of palladium and platinum gave trimethylsilylmethylallyl complexes,[1] equation (2), and no tmm complexes could be isolated. The synthesis of the trimethylsilylmethylallyl palladium complex (**2**) is of interest since it is one of the intermediates implicated in the generation of the catalytic species $[\mathrm{Pd}(\eta^3\text{-tmm})(\mathrm{PPh_3})_2]$ formed in the reaction of the allylic acetate (**1c**) with a palladium(0) complex. In the presence of an electron deficient alkene a metal catalysed cycloaddition of the tmm results,[5] equation (3).

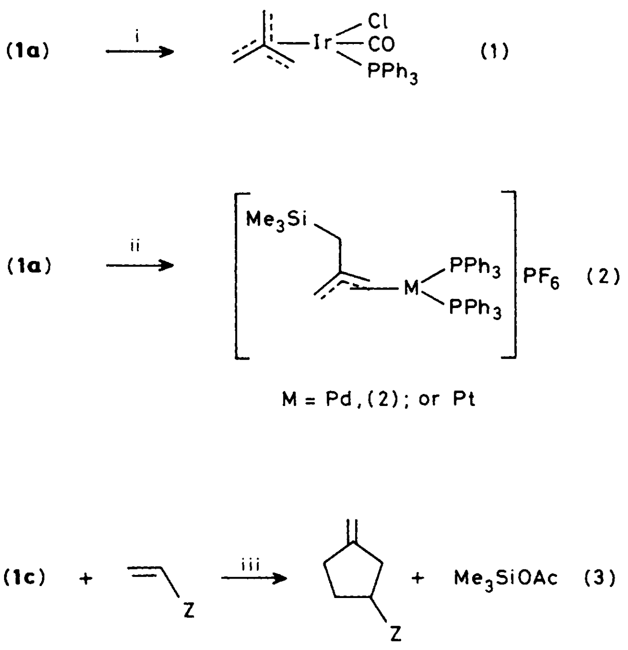
Encouraged by the high reactivity of the allylic mesylate (**1a**) and the good yields of the η^4-tmm complexes isolated we have now investigated the cycloaddition reactions of the tmm equivalent (**1a**) in the presence of various d^8 and d^{10} metal complexes.

No cycloadduct was isolated from the reactions of the mesylate (**1a**) with alkenes in the presence of the d^8 metal complexes *trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]$, $[\mathrm{RhH(PPh_3)_4}]$, $[\mathrm{RhCl(PPh_3)_3}]$, and $[\mathrm{RuH_2(PPh_3)_4}]$. However we have found that the mesylate (**1a**) reacts in the presence of the d^{10} complex $[\mathrm{Ni}\{\mathrm{P(OEt)_3}\}_4]$ to afford a catalysed cycloaddition of tmm to imines and electron deficient alkenes in high yield. The cycloaddition of tmm to imines is also catalysed by a palladium(0)–triethylphosphite complex. The general reaction is shown in Scheme 1 and Table 1 summarises the results.

The reactions involve mixing the mesylate (**1a**) with an excess of the alkene or imine in toluene with 5 mol% of the catalyst. Interestingly $[\mathrm{Pd(PPh_3)_4}]$, which was so effective in catalysing the cycloaddition of tmm to alkenes,[5] was a poor catalyst for the cycloaddition of tmm to imines (entries 8 and 9). This shows that the choice of ligand is an important factor

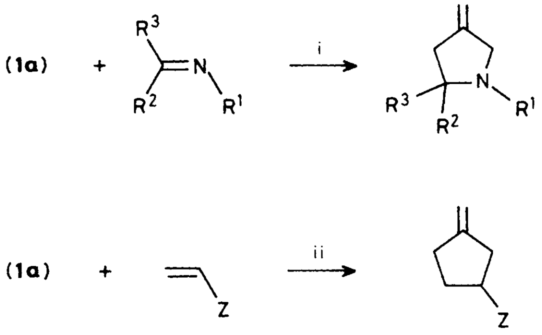


(1)a; X = $OS(O)_2Me$
b; X = Cl
c; X = OCOMe



Z = electron-withdrawing group

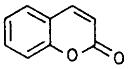
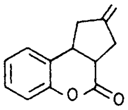
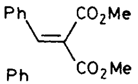
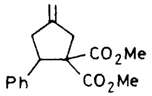
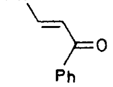
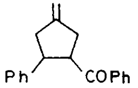
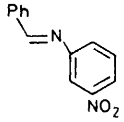
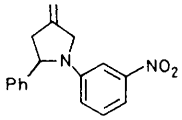
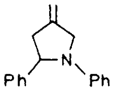
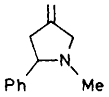
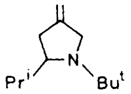
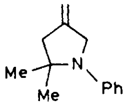
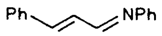
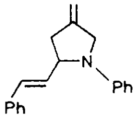
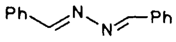
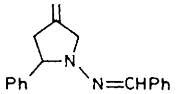
Reagents: i, *trans*-$[IrCl(CO)(PPh_3)_2]$; ii, $[Pd(PPh_3)_4]$ or $[Pt(\textit{trans}\text{-stilbene})(PPh_3)_2]$, NH_4PF_6; iii, cat., $[Pd(PPh_3)_4]$.



Z = electron-withdrawing group

Scheme 1. *Reagents:* i, cat., $[ML_4]$, M = Ni or Pd, L = $P(OEt)_3$, toluene, reflux; ii, cat., $[Ni\{P(OEt)_3\}_4]$, toluene, reflux.

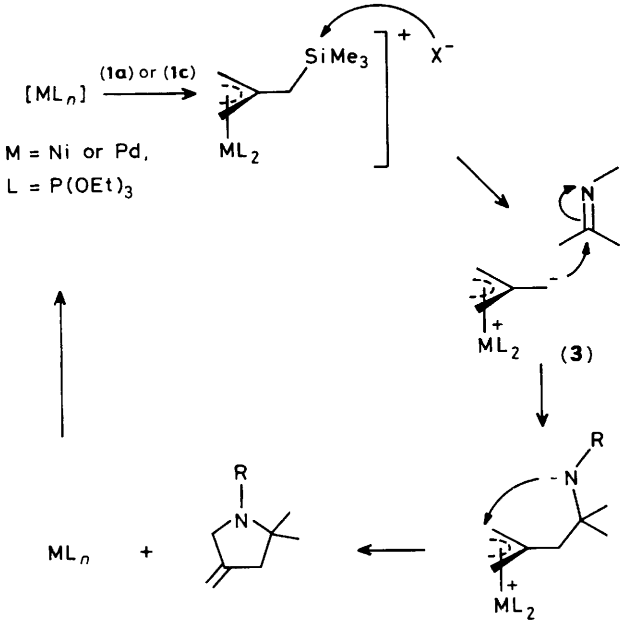
Table 1.

Entry	Acceptor	Reagent	Catalyst	Adduct	Yield, %
1		**(1a)**	(A)		77
2		**(1a)**	(A)		87
3		**(1a)**	(A)		50
4		**(1a)**	(A)		58
5	PhCH=NPh	**(1a)**	(A)		77
6	"	**(1a)**	(B)	"	52
7	"	**(1c)**	(B)	"	73
8	"	**(1c)**	(C)	"	27
9	"	**(1a)**	(C)	"	19
10	PhCH=NMe	**(1a)**	(A)		68
11	$Pr^iCH=NBu^t$	**(1a)**	(A)		50
12	$PhN=CMe_2$	**(1a)**	(A)		40
13		**(1a)**	(A)		69
14		**(1a)**	(B)		55

[a] (A) = $[Ni\{P(OEt_3\}_4]$; (B) = $[Pd_2(dba)_3{\cdot}CHCl_3]$–$8P(OEt)_3$; (C) = $[Pd(PPh_3)_4]$.

in these cycloaddition reactions. Preliminary studies show that the platinum system $[Pt(dba)_2]$–$4P(OEt)_3$ (dba = dibenzylideneacetone) is a poor catalyst for these cycloaddition reactions. The cycloaddition of tmm to imines shows excellent chemoselectivity. Surprisingly no cycloaddition of tmm to the C=C double bond of an α,β-unsaturated imine was detected (entry 13), and the reaction of the mesylate (**1a**) with dibenzylidenehydrazine led to a [3 + 2] cycloaddition and no [3 + 4] adduct was observed (entry 14).

The allylic acetate (**1c**) also serves as a tmm equivalent for the cycloaddition to imines in the presence of palladium catalysts (entries 7 and 8). The mechanism for the reactions of (**1a**) and (**1c**) with both nickel and palladium complexes presumably proceeds *via* a zwitterionic intermediate (**3**) as illustrated in Scheme 2. The inability of d^8 metal complexes to catalyse the addition of tmm to an alkene or imine is presumably due to the formation of an $[ML_3(\eta^4\text{-tmm})]$ complex in which all three methylene carbons are strongly



Scheme 2

co-ordinated to the metal centre,[3] a situation which does not occur upon co-ordination of tmm to a d^{10} ML$_2$ fragment (M = Ni, Pd, or Pt), since slippage to an η^3-tmm complex is electronically favoured.[6] Interestingly an η^4-tmm complex of nickel(0) has been claimed as a reactive intermediate in the codimerisation of methylenecyclopropane with alkenes.[7]

A general procedure for the cycloaddition reaction involved charging a 25 cm^3 flask with a solution of 5 mol% of [Ni{P(OEt)$_3$}$_4$][8] or [Pd$_2$(dba)$_3$·CHCl$_3$]–8P(OEt)$_3$, the imine (2.5 mol. equiv.) and (**1a**) (1 mol. equiv.) in toluene (5 cm^3). The yellow solution was refluxed overnight.

Synthetically this one-step procedure represents an improvement in yield, cleanliness, and convenience in comparison to the earlier two-step synthesis of 4-methylenepyrrolidine which used a more expensive tin reagent.[2] The use of the readily available nickel(0) catalyst to mediate these cycloaddition reactions is also attractive in comparison to the more expensive palladium complexes.

We thank Antoinette Bathgate for experimental assistance, Moira Robinson for high field n.m.r. measurements, the S.E.R.C. for financial support, and Johnson Matthey plc for the generous loan of palladium salts.

Received, 19th May 1986; Com. 666

References

1 M. D. Jones and R. D. W. Kemmitt, *J. Chem. Soc., Chem. Commun.*, 1985, 811.
2 B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1.
3 M. D. Jones, R. D. W. Kemmitt, A. W. G. Platt, D. R. Russell, and L. J. S. Sherry, *J. Chem. Soc., Chem. Commun.*, 1984, 673.
4 M. D. Jones, R. D. W. Kemmitt, and A. W. G. Platt, *J. Chem. Soc., Dalton Trans.*, 1986, 1411.
5 B. M. Trost and D. M. T. Chan, *J. Am. Chem. Soc.*, 1983, **105**, 2315, 2326.
6 T. A. Albright, *J. Organomet. Chem.*, 1980, **198**, 159.
7 R. Noyori, M. Yamakawa, and H. Takaya, *Tetrahedron Lett.*, 1978, 4823.
8 M. Meier and F. Basolo, *Inorg. Synth.*, 1972, **13**, 112.