

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

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

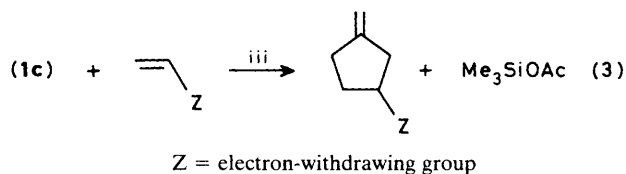
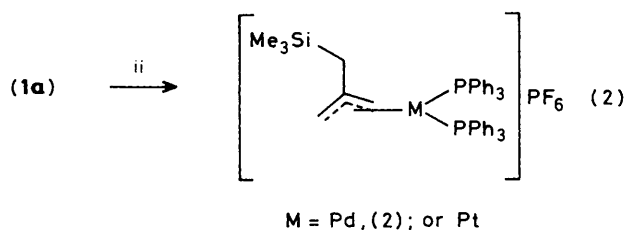
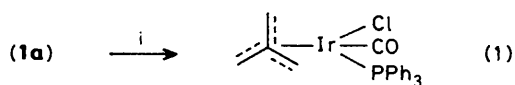
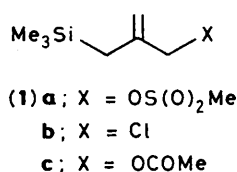
Current interest in metal complexes of trimethylenemethane (tmm)¹ and palladium mediated cycloaddition of tmm to C=C and C=O double bonds² prompts us to report the first metal catalysed additions of tmm to the C=N double bond using a readily available nickel(0) complex $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$.

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 $[\text{Pd}(\eta^3\text{-tmm})(\text{PPh}_3)_2]$ 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).

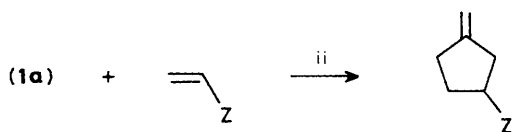
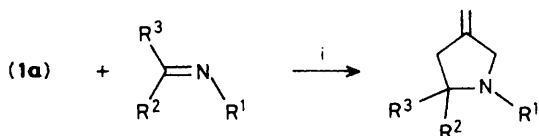
Encouraged by the high reactivity of the allylic mesylate (**1a**) and the good yields of the η^4 -tmm complexes isolated we have now investigated the cycloaddition reactions of the tmm equivalent (**1a**) in the presence of various d^8 and d^{10} metal complexes.

No cycloadduct was isolated from the reactions of the mesylate (**1a**) with alkenes in the presence of the d^8 metal complexes *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, $[\text{RhH}(\text{PPh}_3)_4]$, $[\text{RhCl}(\text{PPh}_3)_3]$, and $[\text{RuH}_2(\text{PPh}_3)_4]$. However we have found that the mesylate (**1a**) reacts in the presence of the d^{10} complex $[\text{Ni}\{\text{P}(\text{OEt})_3\}_4]$ 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 $[\text{Pd}(\text{PPh}_3)_4]$, 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



Reagents: i, *trans*-[IrCl(CO)(PPh₃)₂]; ii, [Pd(PPh₃)₄] or [Pt(*trans*-stilbene)(PPh₃)₂], NH₄PF₆; iii, cat., [Pd(PPh₃)₄].



Z = electron-withdrawing group

Scheme 1. Reagents: i, cat., [ML₄], M = Ni or Pd, L = P(OEt)₃, toluene, reflux; ii, cat., [Ni{P(OEt)₃}₄], toluene, reflux.

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

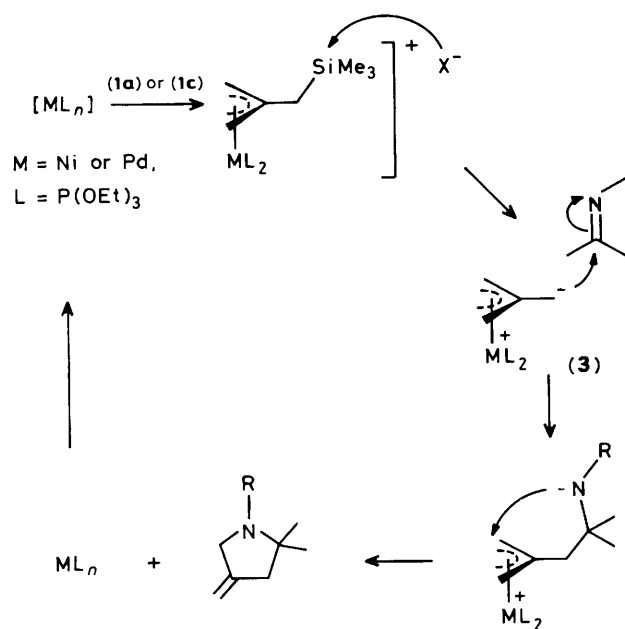
Table 1.

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 ⁱ CH=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) = [Pd₂(dba)₃·CHCl₃]-8P(OEt)₃; (C) = [Pd(PPh₃)₄].

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 d⁸ metal complexes to catalyse the addition of tmm to an alkene or imine is presumably due to the formation of an [ML₃(η⁴-tmm)] complex in which all three methylene carbons are strongly



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 ($M = Ni, Pd, \text{ or } Pt$), 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 cm³ flask with a solution of 5 mol% of $[Ni\{P(OEt)_3\}_4]^8$ or $[Pd_2(dba)_3 \cdot CHCl_3] \cdot 8P(OEt)_3$, the imine (2.5 mol. equiv.) and (1a) (1 mol. equiv.) in toluene (5 cm³). 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.

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