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Preliminary communication

SYNTHESIS OF TRANSITION METAL—HETEROCYCLIC CARBENE COMPLEXES. OXAZOL-2-YLIDENE AND OXAZOLIDIN-2-YLIDENE COMPLEXES OF OSMIUM(II) DERIVED FROM COORDINATED TOSYLMETHYLISOCYANIDE

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Summary

Tosylmethylisocyanide, when coordinated to osmium(II), reacts with aldehydes and ketones in the presence of sodium methoxide, to produce oxazol-2-ylidene and oxazolidin-2-ylidene complexes.

Several synthetic approaches to heterocyclic carbene complexes have been reported. These include the reaction of hydridocarbonylmetal anions with imidazolium salts [1], reaction of electron-rich olefins with suitable platinum metal complexes [2], and the oxidative addition of 2-halo-*N*-methylthiazolium salts to low-valent species [3]. A recent report describes the spontaneous ring-closing reaction of 2-hydroxyethylisocyanide on palladium and platinum leading to oxazolidin-2-ylidene complexes [4]. We describe here a synthesis in which the carbene ring is five-membered, either saturated or unsaturated, and has nitrogen and oxygen as hetero atoms.

Tosylmethylisocyanide, together with other compounds which have the potential for forming α-metalated isocyanides are useful for the synthesis of heterocycles [5], e.g. tosylmethylisocyanide reacts with aldehydes giving oxazoles unsubstituted in the 2-position [6]. When coordinated in metal complexes similar reactions should lead to carbene complexes. To investigate this possibility we chose kinetically inert complexes of osmium(II), thus avoiding reactions at the metal and restricting reactions to the tosylmethylisocyanide ligand.

Both neutral and cationic complexes of tosylmethylisocyanide (TMIC) were prepared and studied. $OsHCl(CO)(TMIC)(PPh_3)_2$ (I) results from reaction of $OsHCl(CO)(PPh_3)_3$ with one equivalent of TMIC and further reaction of I with perchloric acid followed by CO gives $[OsCl(CO)_2(TMIC)(PPh_3)_2]ClO_4$ (II). IR and ^1H NMR data for compounds I and II and other compounds described herein are included in Table 1.

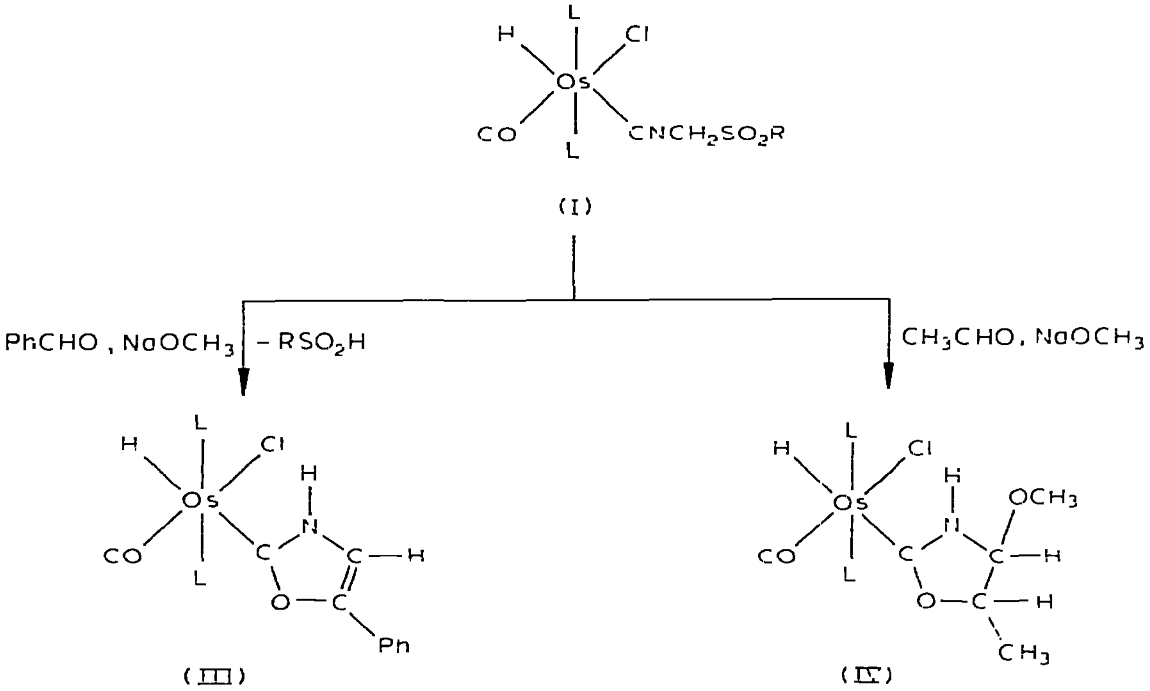
TABLE 1

IR^{a} (cm^{-1}) AND ^{1}H NMR^{b} (τ) DATA FOR OSMIUM(II) CARBENE COMPLEXES AND PRECURSORS

Complex^{c}	ν(CO)	ν(CN)	ν(NH)	ν(SO)	Chemical shifts^{d}
$OsHCl(CO)(TMIC)(PPh_3)_2$ (I)	1945	2140		1335,1145	Os—H, 14.7t^{c}
$[OsCl(CO)_2(TMIC)(PPh_3)_2]^+$ (II)	2080,2015	2210		1330,1140	
$OsHCl(CO)(\overline{CNHCH{=}CPhO})(PPh_3)_2$ (III)	1920		3290		Os—H, 15.73t^{e}, N—H, 0.0s, (exchanges D_2O); CH=C, 3.8d^{f}
$OsHCl(CO)(\overline{CNHCH(OCH_3)CH(CH_3)O})(PPh_3)_2$ (IV)	1915		3320		Os—H, 15.66t^{g}; N—H, 1.1s, CH—CH, 6.0m; OCH_3, 7.14s; CH_3, 9.2d^{h}
$OsCl(\overline{C{=}NCH(SO_2R)CH(CH_3)O})(CO)_2(PPh_3)_2$ (V)	2025,1955			1300,1140	CH—CH, 6.0m; CH_3(tolyl), 7.57s; CH_3, 9.10d^{h}
$[OsCl(\overline{CO)_2(CNHCH(SO_2R)CH(CH_3)O})(PPh_3)_2]^+$ (VI)	2080,2010		3300	1310,1140	N—H, 0.5(br); CH(tosyl), 5.97d^{i}; CH(CH_3), 4.93m; CH_3(tolyl), 7.57s; CH_3, 9.34d^{h}

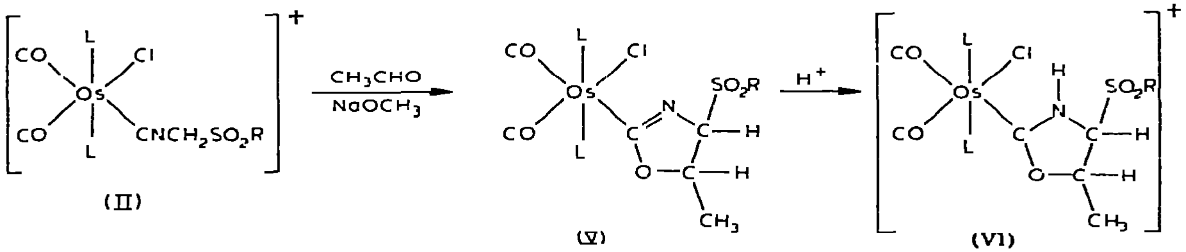
^{a}Nujol mulls. ^{b}$CDCl_3$ solution. ^{c}All compounds reported have satisfactory elemental analyses. ^{d}s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. ^{e}J(P—H) 20 Hz. ^{f}J(H—H) 2 Hz (singlet in D_2O). ^{g}J(P—H) 22 Hz. ^{h}J(H—H) 6 Hz. ^{i}J(H—H) 8 Hz.

I undergoes a rapid and high yield reaction with benzaldehyde in the presence of one equivalent of sodium methoxide producing the oxazol-2-ylidene complex III,and eliminating toluene-*p*-sulphinic acid (see Scheme 1). In contrast, the same reaction with acetaldehyde produces the carbene complex with a saturated ring i.e. an oxazolidin-2-ylidene ligand with the tosyl group replaced by methoxide. Similar substitution of the ring by alkoxide has been reported for oxazolidine synthesis from free TMIC using thallium alkoxide as catalyst [7].



SCHEME 1. L = PPh$_3$, R = *p*-tolyl.

Reaction of cation II with acetaldehyde and sodium methoxide yields a third type of ring system (see Scheme 2).



SCHEME 2. L = PPh$_3$, R = *p*-tolyl.

When one equivalent of methoxide is used as catalyst the carbene ring is deprotonated at N leaving a neutral osmium II complex (V) with an oxazolidin-

2-yl ligand. Protonation produces complex VI with the sulphinate-substituted carbene ring.

Comp. I also reacts with acetone to form $\mathrm{OsHCl(CO)[\overline{COC(CH_3)_2CH(OCH_3)NH}](PPh_3)_2}$ but this reaction is much slower (2 h reflux in CH_2Cl_2) and no reaction has been observed with acetophenone or benzophenone.

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