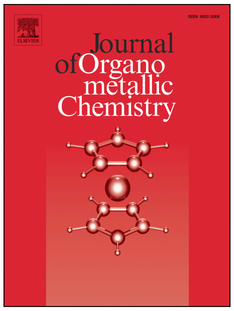

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Ruthenium(II) Pentamethylcyclopentadienyl Half-Sandwich Carbene Complexes with Polypyridyl Ligands

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Abstract: Polypyridyl complexes [RuCl(η^5-C_5Me_5)(N–N)] (**1–4**) [N–N = 2,2'-bipyridine (bpy) (**1**), 4,4'-dimethyl-2,2'-bipyridine (4,4'-Me_2bpy) (**2**), 1,10-phenanthroline (phen) (**3**) and 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen) (**4**)] were prepared by reacting [$RuCl_2$(η^5-C_5Me_5)]$_2$ with Zn dust in the presence of polypyridyl ligands. Unlike the related [RuCl(η^5-C_5Me_5)(L1)(L2)]$^+$ [L1, L2 = P(OR)$_3$, PPh$_3$] derivatives with P-donor ligands, treatment of chloro compounds **1–4** with diazoalkanes Ar1Ar2CN$_2$ afforded polypyridyl carbene complexes [Ru(η^5-C_5Me_5)(=CAr1Ar2)(N–N)]BPh$_4$ (**5–8**) [Ar1 = Ar2 = Ph (**a**), Ar1 = Ph, Ar2 = *p*-tolyl (**b**)]. Comparative DFT studies of the formation of metallacarbenes from aromatic diazoalkanes are reported. Phosphite complex [Ru(η^5-C_5Me_5)(bpy){P(OEt)$_3$}]BPh$_4$ (**9**) and acetylide derivatives [Ru(η^5-C_5Me_5)(C≡CAr)(bpy)] (**10, 11**) [Ar = Ph (**10**), *p*-tolyl (**11**)] were also obtained by substitution of the carbene in **5–8**. Unstable vinylidene cations [Ru(η^5-C_5Me_5){=C=C(H)Ar](bpy)]$^+$ (**12, 13**) were formed by protonation with HBF$_4$•Et$_2$O of acetylide species **10, 11**. The complexes were characterized spectroscopically (IR and ^{1}H, ^{13}C, ^{31}P NMR) and by X-ray crystal structure determination of [Ru(η^5-C_5Me_5){=C(Ph)(*p*-tolyl)}(bpy)]BPh$_4$ (**5b**).

Keywords: Ruthenium; Half-sandwich; Diazoalkane; Carbene; Polypyridyl; Acetylide

1. Introduction

Diazoalkanes Ar1Ar2CN$_2$ are a class of molecules which may behave as ligands in transition metal chemistry, giving rise to a number of stable and isolable complexes [1-4]. In some cases, diazoalkanes are also reported to react with metal complexes to give metallacarbene derivatives [5,6] after loss of N$_2$.