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Preliminary Communication

NOVEL CYCLIC "YLIDE—CARBENE" COMPLEXES

I. SYNTHESIS OF 3-(DIMETHYLPHENYLPHOSPHORANE)INDOLIDIN-2-YLIDENE COMPLEXES OF PLATINUM(II) DERIVED FROM METAL-COORDINATED PHOSPHONIUM-SUBSTITUTED ISOCYANIDE LIGANDS

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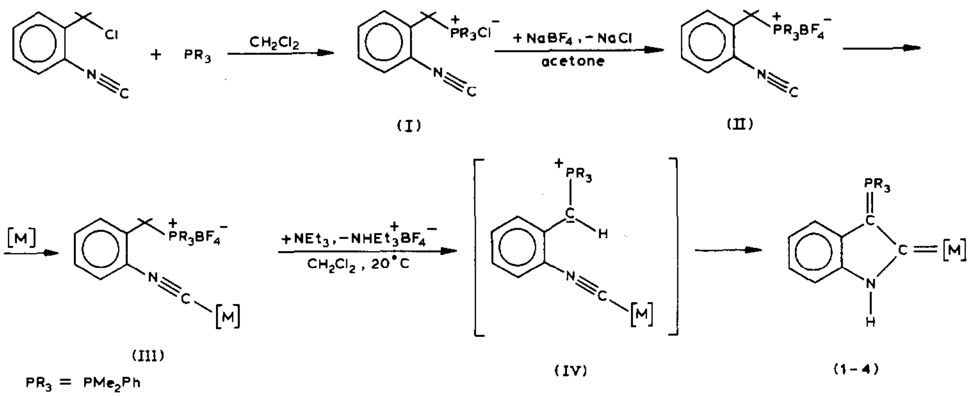
Summary

Nucleophilic attack of NEt_3 on the activated methylene group of the $\text{-}CH_2\overset{+}{P}R_3$ moiety of the platinum(II)-coordinated phosphonium-substituted isocyanides o-$(X^{-}\,{}^{+}PR_3CH_2)C_6H_4NC$ ($X = Cl, BF_4$; $PR_3 = PMe_2Ph$) produces the highly reactive ylide function $—\overset{-}{C}H—\overset{+}{P}R_3$, which rapidly interacts intramolecularly with the metal-coordinated isocyanide group to form novel 5-membered cyclic ylide-substituted complexes of platinum(II) of the general formula $LnPt^{II}{=}\overline{CN(H)C_6H_4C}(PMe_2Ph)$ ($LnPt^{II}$ = *cis*-$PtCl_2(PMe_2Ph)$; *trans*-$PtCl(PR'_3)_2{}^{+}$, $PR'_3 = PPh_3, PMePh_2, PMe_2Ph$).

A major goal of the transition-metal coordination chemistry of functionalized isocyanide ligands is the synthesis of heterocycles [1—6]. This has been achieved by various strategies, one of which involves the formation of cyclic carbenemetal intermediates derived from nucleophilic attack on the metal-coordinated isocyanide ligands [1—3].

We recently reported the synthesis and the interactions with organometallic compounds of functionalized isocyanide ligands of the type o-$(XCH_2)C_6H_4NC$ ($X = Cl, I$) [7,8]. The halomethyl function reacts also with organic substrates such as tertiary monophosphines (PR_3) to yield a new series of phosphonium-substituted isocyanide ligands of the general formula o-$(X^{-}\,R_3\overset{+}{P}CH_2)C_6H_4NC$. The phosphonium group in these ligands can be regarded as a suitable source of the corresponding ylide function [9] o-$(R_3\overset{+}{P}—\overset{-}{C}H)C_6H_4NC$, which may potentially undergo further reactions. Thus, molecular models indicate that



PR$_3$ = PMe$_2$Ph

[M] = *cis*-PtCl$_2$(PR$'_3$) ; PR$'_3$ = PMe$_2$Ph (1)

[M] = $[trans\text{-PtCl(PR}'_3)_2]^+$ BF$_4^-$; PR$'_3$ = PPh$_3$ (2), PMePh$_2$ (3), PMe$_2$Ph (4)

SCHEME 1

the nucleophilic ylide carbon is in a favourable position to interact intramolecularly with the metal-coordinated isocyanide ligand to form a 5-membered cyclic "carbene" complex. In this communication we show how we have exploited this property of phosphonium-substituted isocyanide complexes to prepare new stable ylide-functionalized cyclic "carbene" derivatives of platinum(II) under mildly basic conditions (Scheme 1).

Reactions of equivalent amounts of I [10] with $[\mathrm{PtCl_2(PMe_2Ph)}]_2$ [11] and of II [12] with $[\mathrm{PtCl(PR'_3)_2}]_2(\mathrm{BF_4})_2$ [13] ($\mathrm{PR'_3} = \mathrm{PPh_3}, \mathrm{PMePh_2}, \mathrm{PMe_2Ph}$) give high yields of the mononuclear complexes III. These derivatives show ν(NC) stretchings in the 2185—2200 cm^{-1} range ($\mathrm{CH_2Cl_2}$), suggesting a high electrophilic character for the isocyanide carbon [16] and therefore its potential ability to react with nucleophiles to form carbene complexes [17]. Thus, a fast reaction takes place in $\mathrm{CH_2Cl_2}$ at room temperature upon treatment of complexes III with a 10-fold excess of a mild base such as triethylamine, affording in high yield (ca. 70%) the stable ylide-functionalized "carbene" complexes 1—4. Attack of $\mathrm{NEt_3}$ on the activated methylene group of the $-\mathrm{CH_2\overset{+}{P}R_3}$ phosphonium moiety would produce the highly reactive ylide—isocyanide—metal intermediate, IV, which would rapidly rearrange to the final cyclic "carbene" products via intramolecular nucleophilic attack of the free ylide carbon on the coordinated isocyanide.

The ylide—platinum(II) intermediates IV cannot be observed, probably owing to their high reactivity towards the highly electrophilic isocyanide. It thus appears that under the basic reaction conditions used isocyanide—metal activation is essential for the reaction. Thus the coordinated phosphonium isocyanide in the chromium(0) carbonyl complex $[o\text{-}(\mathrm{Cl^-\,Me_2Ph\overset{+}{P}CH_2})\mathrm{C_6H_4NC}]$-$\mathrm{Cr(CO)_5}$ [18], which displays the ν(NC) stretch at 2133 cm^{-1} ($\mathrm{CH_2Cl_2}$), i.e. about 55—70 cm^{-1} lower than the platinum(II) complexes III, does not form the "ylide—carbene" derivative upon treatment with $\mathrm{NEt_3}$.

All the ylide-substituted "carbene—platinum(II)" complexes 1—4 are air-stable in the solid state and in solution. The *cis* and *trans* stereochemistry of complexes 1 and 2—4, respectively, are assigned by IR, ^{1}H and ^{31}P {^{1}H} NMR

TABLE 1

SELECTED IR, ^{1}H AND ^{31}P $\{^1$H$\}$ NMR DATA FOR THE NEW CYCLIC "CARBENE—YLIDE" COMPLEXES OF PLATINUM(II)

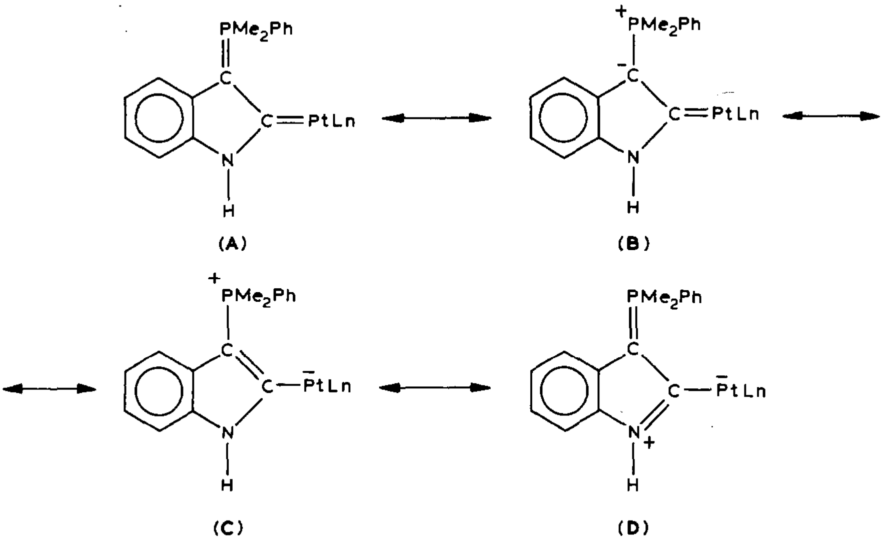
Complex [a]	IR [b] (cm^{-1})		^{1}H NMR [c]			^{31}P $\{^1$H$\}$ NMR [c]	
	ν(N—H)	ν(Pt—Cl)	δ(NH)	δ(P—CH$_3$)$_{ylide}$	δ(P—CH$_3$)$_{metal}$	δ(P)$_{ylide}$	δ(P)$_{metal}$
1	3258(m)	288(m), 271(m)	14.66(d) [d]	2.53(d) [e] 2.48(d) [f]	1.70(d) [g] 1.58(d) [h]	10.12(s) [i]	—18.26(s) [j]
2	3344(m)	300(m)	8.63(d) [k]	2.13(d) [l]		7.20(t) [m]	18.44(d) [n]
3	3361(m)	302(m)	10.30(d) [o]	1.85(d) [p]	1.84(d) [q]	7.44(t) [r]	4.28(d) [s]
4	3348(m)	300(m)	10.38(d) [t]	1.85(d) [u]	1.83(t) [v]	7.57(t) [w]	— 8.42(d) [x]

[a] Satisfactory elemental analyses were obtained for all the complexes. [b] Nujol mull; m, medium. [c] Spectra recorded in DMSO-d_6 (compound 1) and CD_2Cl_2 (compounds 2—4) at +25° C and referenced to Me_4Si (^{1}H) and 85% H_3PO_4 (^{31}P); δ in ppm, J in Hz; negative chemical shifts are upfield from the reference used; s, singlet; d, doublet; t, triplet. [d] ^3J(HPt) 23.0, ^4J(HP) 3.2. [e] ^2J(HP) 14.1. [f] ^2J(HP) 14.4. [g] δ(P—CH$_3$)$_{metal}$; ^2J(HP) 11.5, ^3J(HPt) 44.0. [h] δ(P—CH$_3$)$_{metal}$; ^2J(HP) 11.4, ^3J(HPt) 47.0. [i] ^3J(PPt) 50.7. [j] ^1J(PPt) 4044. [k] ^3J(HPt) 25.0, ^4J(HP) 3.0. [l] ^2J(HP) 13.6. [m] ^3J(PPt) 45.4, ^4J(PP) 1.6. [n] ^1J(PPt) 2700, ^4J(PP) 1.6. [o] ^3J(HPt) 25.0, ^4J(HP) 2.9. [p] ^2J(HP) 13.3. [q] δ(P—CH$_3$)$_{metal}$; ^2J(HP) + ^4J(HP) 7.5, ^5J(HPt) 42.0. [r] ^3J(PPt) 47.2, ^4J(PP) 1.8. [s] ^1J(PPt) 2612, ^4J(PP) 1.8. [t] ^3J(HPt) 25.0, ^4J(HP) 2.8. [u] ^2J(HP) 13.4. [v] δ(P—CH$_3$)$_{metal}$; ^2J(H—P) + ^4J(HP) 8.2, ^3J(HPt) 33.0. [w] ^3J(PPt) 49.3, ^4J(PP) 1.8. [x] ^1J(PPt) 2501, ^4J(PP) 1.8.

spectroscopy (Table 1). Diagnostic spectral features of the "carbene" unit are as follows. The ^{31}P NMR resonance of the ylide phosphorus atom in the neutral complex 1 appears as a sharp singlet flanked by ^{195}Pt satellites (^3J(PPt) 50.7 Hz), whereas it shows up as a triplet (with ^{195}Pt satellites, ^3J(PPt) 45—50 Hz) in the cationic compounds 2—4 owing to coupling with the metal-coordinated phosphine ligands (^4J(PPt) 1.6—1.8 Hz). The N—H signal is observed in the ^{1}H NMR spectra of complexes 1—4 as a broad doublet (with ^{195}Pt satellites) arising from coupling with the ylide phosphorus atom (^4J(HP) ca. 3.0 Hz) rather than with the metal-coordinated phosphorus. Coupling with the latter ligand would give rise to a triplet as a result of coupling with the two magnetically equivalent phosphine ligands in the *trans* complexes 2—4. Further, the magnitude of the ^3J(HPt) coupling constant (ca. 25 Hz) is consistent with a *cis* Pt—C(carbene)—N—H arrangement [19]. All the complexes 1—4 display the ν(NH) stretch in the IR as a medium absorption at 3258—3361 cm^{-1} (Nujol).

The "carbene" moiety and the π interactions with its substituents can be depicted as shown in A—D.

The absence from the IR spectra of compounds 1—4 of the C=N vibration, which is generally observed [2,20] as a medium to strong absorption between 1500—1600 cm^{-1} in aminocarbene complexes of platinum(II), strongly suggests a poor contribution from a structure of type D. No further assessment of the relative contribution of each of the remaining forms A—C to the actual structure of these carbene—platinum(II) species can be made, at least on the basis of the spectroscopic investigation alone. However, X-ray structural determinations carried out on "ylide—carbene" complexes of the type $(CO)_5Cr(OSiMe_3)CHPMe_3$ [21], $Cp(CO)_2MnC(CO_2Me)CHPPh_3$ [22] and $Cp(CO)_2MnC(OMe)C(Me)PMe_3$ [23] have shown that the "vinyl-like" structure C is a better description of the bonding situation in those complexes. These findings, coupled with the observation of the poor π-donor properties



of the LnPt^{II} metal fragments [24], lead to the conclusion that in our system the electronic structure C again predominates over the remaining forms.

There appear to be no precedent in the literature for the interactions of phosphorus ylides with transition-metal isocyanide complexes [25]. The phosphonium-substituted isocyanides described above are functional ligands, with a potential for reaction with a wide range of transition metals and synthetically useful reagents to form novel functionalized "carbene" complexes, whose relevance in organic synthesis has been recently emphasized [26]. Detailed structural determinations of such "ylide—carbene" metal complexes are in progress.

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10 This ligand is prepared in quantitative yield by reaction of *o*-$(ClCH_2)C_6H_4NC$ [7] with a slight molar excess of PMe_2Ph in CH_2Cl_2 at room temperature for 1d. ^1H NMR (80 MHz, $CDCl_3$, Me_4Si as internal reference, δ in ppm, J in Hz): $\delta(CH_2)$ 4.78(d), $^2J(HP)$ 16.1 Hz; $\delta(P—CH_3)$ 2.60(d), $^2J(HP)$ 14.0 Hz. $^{31}P\ \{^1H\}$ NMR (32.2 MHz, $CDCl_3$, H_3PO_4 85% as external reference, δ in ppm): $\delta(P)$ 25.20(s). IR (Nujol): $\nu(NC)$ 2122(s) cm^{-1}. Satisfactory elemental analyses were obtained for this and all the other compounds prepared.
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13 These compounds are prepared in situ by reaction of *cis*-$PtCl_2(PR'_3)_2$ ($PR'_3 = PPh_3$ [14], $PMePh_2$ [15], PMe_2Ph [15]) with 1 equivalent of $AgBF_4$ in CH_2Cl_2.
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18 This compound is obtained by reaction of [*o*-$(ClCH_2)C_6H_4NC]Cr(CO)_5$ [7] with 1.2 equivalents of PMe_2Ph in CH_2Cl_2 at room temperature for 2d (yield 80%). ^1H NMR ($CDCl_3$): $\delta(CH_2)$ 4.61(d), $^2J(HP)$ 16.2 Hz; $\delta(P{-}CH_3)$ 2.51(d), $^2J(HP)$ 14.0 Hz. $^{31}P\ \{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 24.48(s). IR (CH_2Cl_2): $\nu(NC)$ 2133(m), $\nu(CO)$ 2050(s), 2004(m), 1962(s,br) cm^{-1}.

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