Journal of Organometallic Chemistry, 171 (1979) C50—C52

Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF NEW CYCLOPALLADATED CARBENE COMPLEXES

K. HIRAKI*, M. ONISHI* and K. SUGINO

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki (Japan)

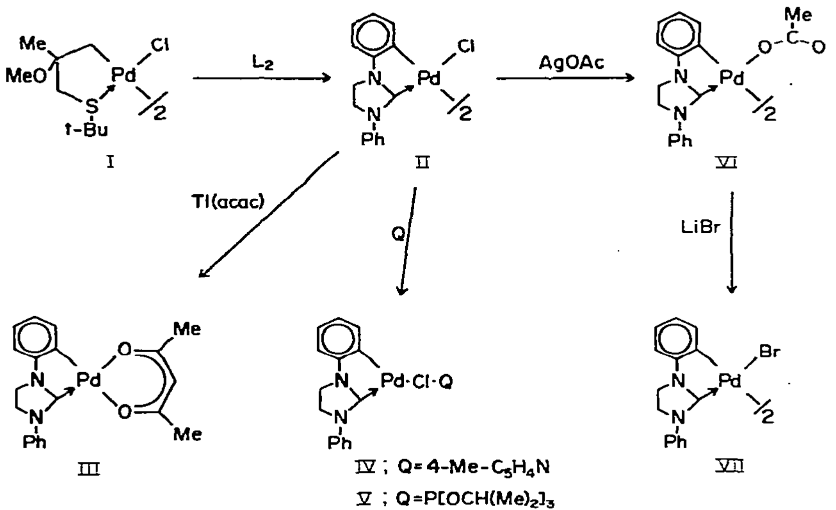
(Received February 21st, 1979)

Summary

Di-μ-chlorobis(2-methyl-2-methoxy-3-t-butylthiopropyl)dipalladium(II) reacted with bis(1,3-diphenyl-2-imidazolidinylidene) to afford a new chloro-bridged carbene complex $[\{PdCl(did)\}_2]$ (did = 1,3-diphenyl-2-imidazolidinylidenato,*2-C,2′-C*) in 46.2% yield, which has a cyclopalladated chelate structure involving a Pd—carbene and a Pd—aryl bond; new carbene complexes, $[\{PdBr(did)\}_2]$, $[\{Pd(CH_3COO)(did)\}_2]$, [Pd(acac)(did)], and [PdCl(did)Q] (Q = 4-MePy, $P[OCHMe_2]_3$) were also prepared from $[\{PdCl(did)\}_2]$.

An electron-rich olefin, bis(1,3-diphenyl-2-imidazolidinylidene, $[=\overline{CN(Ph)CH_2CH_2N}(Ph)]_2$ (L_2) has been used as an organic precursor for the synthesis of transition metal carbene complexes [1,2]. We have recently shown that this olefin reacts with a few cyclopalladated halogen-bridged dimeric complexes which contain a palladium—aryl σ bond to yield mononuclear carbene complexes [3]. In the present study, di-μ-chlorobis(2-methyl-2-methoxy-3-t-butylthiopropyl,*1-C,S*)dipalladium(II) (I) [4] was treated with L_2 and a new dimeric carbene complex was formed.

A mixture of L_2 and I in 1/1 molar ratio was heated in *m*-xylene under reflux for 40 min. The resulting black precipitate was separated and extracted with boiling acetonitrile for 10 h. The extracted solid was washed with dichloromethane to afford pale yellow microcrystals of di-μ-chlorobis(1,3-diphenyl-2-imidazolidinylidenato,*2-C,2′-C*)dipalladium(II) (II). In its IR spectrum two bridging ν(Pd—Cl) bands were observed at 258 and 239 cm^{-1}. The new dimeric complex II reacted with thallium acetylacetonate, 4-methylpyridine, triisopropyl phosphite, and silver acetate to yield complexes III, IV, V and VI, respectively, as shown in Scheme 1. Bridging acetato ligands of VI (Nujol mull) showed two bands at 1560 and 1420 cm^{-1}, and complex VI was treated with LiBr to give the bromo complex VII. These six complexes II—VII were stable in the solid state at room temperature, and their elemental analyses were satisfactory.



SCHEME 1

A ^{13}C-NMR spectrum of III in CD_2Cl_2 exhibited a carbene carbon (2-C) resonance at δ(C) 192.1 ppm from TMS, and a resonance at δ 139.2 ppm assigned to the palladium-substituted *o*-phenylene carbon (2′-C)*. Two resonances at δ 140.3 and 149.2 ppm are assignable to a *N*-substituted carbon (1′-C) of the *o*-phenylene group and to that (1″-C) of the unmetallated phenyl group, respectively. Two oxygen-bonding carbons of the acetylacetonato ligand resonated at δ 187.5 abd 186.5 ppm, and the two methyl carbon resonances appeared at δ 28.0 and 27.3 ppm, indicating non-equivalence of the two coordination sites of the acetylacetonato ligand, due to the cyclopalladation of the carbene ligand. In addition, a mass spectrum of III exhibited a parent-ion isotope pattern centered at *m/e* 426 in accord with the proposed structure. Complex III showed C=O and C=C stretching bands characteristic of the enolate chelate.

A ^{13}C NMR spectrum of V was recorded in $CDCl_3$, and it showed two doublets at δ 138.5 ppm (*J* 10.7 Hz) for a palladium-substituted o-phenylene carbon and at δ 200.6 ppm (*J* 205.1 Hz) for a carbene carbon atom. The relatively small coupling constant of the former carbon with the ^{31}P nucleus of the triisopropyl phosphite ligand and a fairly large coupling constant of the latter carbon indicate that the triisopropyl phosphite ligand is located *trans* to the carbene carbon [5]. Two *N*-substituted aromatic carbons showed signals at δ 140.7 and 150.2 ppm, similar to those of III.

The ^{1}H NMR spectra of III, IV, V and VI showed a pattern characteristic of the cyclopalladated *o*-phenylene group in the range δ 8.6—6.4 ppm, and an AA′BB′ multiplet for the methylene groups of the 2-imidazolidinylidene ligand in the range δ 4.3—4.2 ppm.

The IR spectra of the six carbene complexes showed a strong band near 1280 cm^{-1} for ν(N—C(aromatic)) of the carbene ligand, and a medium band at ca. 1480–1500 cm^{-1} for ν(N—C(carbene)) [2]. Moreover, an additional sharp band at ca. 750 cm^{-1}, which was absent in the olefin L_2, was tentatively assigned to an *ortho*-disubstituted phenylene group in the carbene ligand.

---

*Assignments of these quaternary carbons were accomplished by comparison with the spectra of complex V and related molecules [3,5].

TABLE 1

SYNTHESES AND PROPERTIES OF NEW CARBENEPALLADIUM COMPLEXES

Complex	Reaction [a]		Yield [b] (%)	Color	M.p. (dec) (°C)	^{1}H-NMR data [e]	
	Solvent	Time (h)				CH_3	CH
II	*m*-Xylene	0.7	46.2 [c]	Pale yellow	> 300	[f]	
III	Benzene	2	64.1	Off white	225	1.36(s) 1.96(s)	5.20(s)
IV	THF	2.5	24.5	Off white	212	2.15(s)	
V	THF	5	76.3	Yellow	180	1.33(d) [g,h]	5.0(c) [g]
VI	Acetone	1	75.1	Yellow	189—202	1.27(s)	
VII	Methanol	6	100.0 [d]	Pale yellow	246—254	[f]	

[a] Under reflux. [b] Based on II, unless noted elsewhere. [c] Based on I. [d] Based on VI. [e] δ Values from TMS. Resonances for protons in the cyclopalladated carbene ligand and aromatic protons are omitted. Abbreviations used; s, singlet, d, doublet; c, complex. In CD_2Cl_2, unless noted elsewhere. [f] NMR spectrum was not obtained owing to low solubility. [g] In $CDCl_3$. [h] $J(^{31}P—^1H)$ 6.7 Hz.

On the basis of these results, the complexes obtained in this study are characterized as new complexes containing a cyclopalladated chelate structure within the carbene ligand. It seems likely that a halogen-bridge splitting reaction of I with L_2 gave an intermediate carbene complex which retains the 2-methyl-2-methoxy-3-t-butylthiopropyl group, and that the latter then abstracted immediately an *ortho*-proton from a phenyl ring attached to the 2-imidazolidinylidene ligand and was eliminated. In the formation reaction of the carbene complexes, the cleavage of the palladium—alkyl σ bond showed a sharp contrast to the retention of the palladium—aryl σ bond as described previously [3]. Similar *ortho*-metallation of a 1,3-di-*p*-tolyl-2-imidazolidinylidene ligand occurred in a carbeneruthenium(II) complex reported by Lappert and coworkers [6].

Preliminary studies suggest that dicarbene complexes involving the cyclopalladated carbene ligand and an unmetallated carbene ligand, were obtained by a cleavage reaction of the halogen-bridge bonds in II and VII with L_2.

Acknowledgement

We thank Mr. Jun Saito, Mitsui Toatsu Chemicals, Inc., Yokohama-shi, for helpful discussions on ^{13}C NMR spectra.

References

1 D.J. Cardin, B. Çetinkaya, E. Çetinkaya and M.F. Lappert, J. Chem. Soc., Dalton, (1973) 514.
2 M.F. Lappert, J. Organometal. Chem., 100 (1975) 139.
3 K. Hiraki, M. Onishi, K. Sewaki and K. Sugino, Bull. Chem. Soc. Japan, 51 (1978) 2548.
4 Y. Takahashi and A. Tokuda, J. Organometal. Chem., 35 (1972) 415.
5 D.J. Cardin, B. Çetinkaya, E. Çetinkaya and M.F. Lappert, J. Chem. Soc., Dalton, (1973) 1982.
6 P.B. Hitchcock, M.F. Lappert and P.L. Pye, J. Chem. Soc., Chem. Commun., (1977) 196.