Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Interaction of platinum(0) with cyclopropenones

J.P. VISSER and J.E. RAMAKERS-BLOM

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.) (The Netherlands)

(Received September 14th, 1972)

SUMMARY

Platinum(0) can be inserted into a carbon–carbon single bond of cyclopropenones.

In previous papers we have reported that double-bond coordination of (hetero)-cyclopropenes to platinum(0) saturates the ring system[1,2]. Since the reactivity of cyclopropanones is markedly different from, and in most instances greater than, that of cyclopropenones[3], we thought that coordination of cyclopropenones might effect a change in reactivity. Bird and co-workers[4] observed that $Co_2(CO)_8$ and $Fe_3(CO)_{12}$ catalysed the conversion of cyclopropenones into acetylenes, whereas with $Ni(CO)_4$ in the presence of water acrylic acids were formed.

Reaction of methylcyclopropenone with bis(triphenylphosphine)(ethylene)platinum in $CDCl_3$ at −65° proceeded with exchange of ethylene to yield the expected complex I. The chemical shifts and the ^{195}Pt–H and P–H spin–spin constants in the NMR spectrum of I are indicative of coordination to the carbon–carbon double bond[2]. Complex I was isolated as a crystalline material upon additions of pentane to the reaction mixture in toluene. In solution at −30° the platinum atom was inserted into a carbon–carbon single bond to yield II. In the solid state, the conversion of I to II occurred slowly at room temperature.

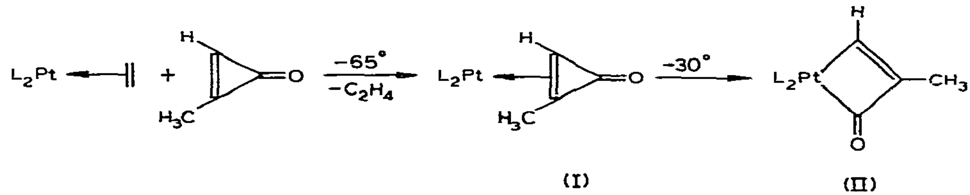
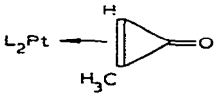
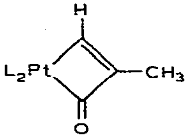
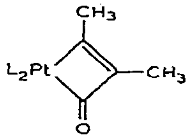
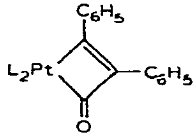


TABLE 1

CHARACTERISTICS IR[a] AND NMR[b] ABSORPTIONS AND COUPLING CONSTANTS OF COMPLEXES I–IV

		$\nu(C{=}C)$ (cm^{-1})	$\nu(C{=}O)$ (cm^{-1})	H			CH_3		
				δ (ppm)	J(P–H) (Hz)	J(Pt–H)[c] (Hz)	δ (ppm)	J(P–H) (Hz)	J(Pt–H)[c] (Hz)
	(I)		1750 vs	3.71	7.5	53.5	1.43	6.5	25.5
	(II)	1675 s	1640 vs		d		1.57	0	13
	(III)	1660 s	1640 vs				1.55 1.18	0 6	13 47.5
	(IV)		1655 vs						

[a] KBr discs.
[b] in $CDCl_3$; ppm downfield from TMS (internal standard).
[c] ^{195}Pt in 33.8% natural abundance.
[d] Masked by phenyl resonance

We have investigated the reactivity of coordinated methylcyclopropenone in reactions characteristic of methylcyclopropanone, namely with methanol, sulphur dioxide and several *cis*-dienes[3]. In all cases rearrangement to II was faster than the intended reaction with the ligand.

Dimethyl- and diphenylcyclopropenone[★] also reacted with bis(triphenylphosphine)-(ethylene)platinum, but only to give the insertion products III and IV respectively. With low temperature NMR and IR spectroscopy no traces of olefin complexes similar to I were detected.

Data on the structure of the insertion products are provided by their IR and NMR spectra (see Table 1). The IR spectra of the methyl-substituted products (II and III) exhibit

---

[★] After this paper was prepared, a communication appeared describing the synthesis and crystal structure of IV[7]. The reported results are in accord with those described here.

two absorption bonds in the double-bond stretching region; the bond at 1640 cm^{-1} is attributed to the ν(C=O) and the bond at higher frequency to the ν(C=C). The ν(C=O) is in the region characteristic of carbonyl groups attached to Pt^{II} [5,6]. The position of the methyl group in II was established by comparing its NMR spectrum with that of III. The chemical shifts and the ^{195}Pt–H and P–H coupling constants of the methyl in II are similar to those of the low-field methyl in III. The large J(P–H)(6Hz) of the high-field methyl group in III indicates that this group must be located next to the platinum atom.

Bird suggested that similar insertion products are formed as intermediates in the decomposition of diarylcyclopropenones with complexes of Fe^0, Co^0 and Ni^0. The platinum insertion products (II–IV), however, were thermally very stable and did not produce acetylenes when heated in solution or in the solid state.

The above-described coordination and insertion reactions were not observed with tetrakis(triphenylphosphine)palladium.

REFERENCES

1 J.P. Visser, A.J. Schipperijn, J. Lukas, D. Bright and J.J. de Boer, *Chem. Commun.*, (1971) 1266.
2 J.P. Visser, C.G. Leliveld and D.N. Reinhoudt, *Chem. Commun.*, (1972) 178.
3 N.J. Turro, *Acc. Chem. Res.*, 2 (1966) 25.
4 C.W. Bird, E.M. Briggs and J. Hudec, *J. Chem. Soc. (C)*, (1967) 1862; C. Ayray, C.W. Bird, E.M. Briggs and A.F. Harmer, *Organometal. Chem. Synt.*, 1 (1971) 187.
5 R. Ugo, *Coord. Chem. Rev.*, 3 (1968) 319.
6 T. Kobayashi, Y. Takahashi, S. Sakai and Y. Ishii, *Chem. Commun.*, (1968) 1373.
7 W. Wong, S.J. Singer, W.D. Pitts, J.F. Watkins and W.H. Baddley, *Chem. Commun.*, (1972) 672.