Nuclear Magnetic Resonance and Structural Studies of Rhodium–Diarylcarbene Complexes

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Summary ^{13}C N.m.r. and single-crystal *X*-ray studies of $[Rh(CPh_2)Cl(C_5H_5N)]_2CO$, $[Rh(CPh_2)(\pi\text{-}C_5H_5)]_2CO$, and $[Rh(CPh_2)(\pi\text{-}C_5H_5)]_2$ indicate that the CPh_2 groups occupy bridging positions in these three molecules.

Recently the syntheses of some novel rhodium diphenylcarbene complexes using diphenyldiazomethane or diphenylketen as the carbene source were reported.[1] Reaction of $[Rh(CO)_2Cl]_2$ with diphenyldiazomethane produced

$[Rh(CO)(CPh_2)Cl]_n$ (I) which seems to be polymeric because of its insolubility in most solvents. Treatment of (I) with pyridine formed $[Rh(CPh_2)Cl(C_5H_5N)]_2CO$ (II)† and reaction of (I) with NaC_5H_5 gave $(\pi\text{-}C_5H_5)_2Rh_2(CPh_2)_2CO$ (III). Heating complex (III) in solution caused loss of CO and formation of $(\pi\text{-}C_5H_5)_2Rh_2(CPh_2)_2$ (IV). We report here the unusual structures of (II), (III), and (IV) based on single-crystal *X*-ray and ^{13}C n.m.r. studies of these molecules

TABLE. ^{13}C N.m.r. data of the rhodium carbene complexes

Compound	Chemical shift	$J(^{103}Rh\text{-}^{13}C)$	Assignment
(II)	206·5	47·3(t)	CO
	185·2	18·1(t)	Carbene-C
(III)	223·4	42·4(t)	CO
	156·0	23·3(t)	Carbene-C
	130·7, 129·6, 128·1, 126·7, 126·0, 125·0 123·9		Ph
(IV)	188·2	42·7(t)	Carbene-C
	131·3, 128·1, 126·2, 124·6		Ph

[a] CH_2Cl_2 solvent, p.p.m. from $Me_4Si = 0$.

The ^{13}C n.m.r. spectra of (II), (III), and (IV) containing natural abundance ^{13}C, in the presence of 0·03M $Cr(acac)_3$, showed no signals attributable to the carbonyl or carbene carbon atoms. However, use of 20% ^{13}C-enriched $Ph_2\text{-}^{13}CN_2$ in the preparation of compounds (II), (III), and (IV) as described above allowed observation and assignment of the carbene carbon resonances, and use of 60% ^{13}C-enriched $[Rh(^{13}CO)_2Cl]_2$ allowed observation and assignment of the carbonyl carbon resonances (see Table). Both the carbonyl and carbene resonances of (II) appear as sharp triplets at room temperature and at −85°, suggesting that the two carbene ligands and the carbonyl group are in bridging positions between the two rhodium atoms. Furthermore the chemical shift and $J(^{103}Rh\text{-}^{13}C)$ values for the carbonyl carbon of (II) are similar to the values obtained for the bridging carbonyl groups of $(C_5H_5)_2Rh_2(CO)_3$[2] and $Rh_4(CO)_{12}$.[3] These ^{13}C n.m.r. values are distinctively different from those of terminal carbonyl groups. Since these data lead to an unusual structure for (II), we have undertaken a single-crystal *X*-ray study to confirm our results. Preliminary results indicate that the material crystallizes in the monoclinic space group *C*2 (C_2^3) with $a = 19{\cdot}14(1)$, $b = 10{\cdot}05(1)$, $c = 11{\cdot}41(1)$ Å, $\beta = 121{\cdot}17(3)°$, $U = 1912(2)$ Å^3. The calculated density for two $[Rh(CPh_2)Cl(C_5H_5N)]_2CO,2CH_2Cl_2$ units per unit cell was in agreement with the observation that the solid would sink in CCl_4 and float in EtI although we were unable to obtain an accurate observed density because of the high solubility of the solid. Selection of the non-unique space group *C*2 was made by the Patterson method and subsequent successful structure refinement. At the present stage of least-squares refinement based on 1831 reflections, the residual, *R*, is 0·07. The structure is given in the Figure. The molecule contains two-fold symmetry such that the carbonyl group lies on a crystallographic two-fold axis.

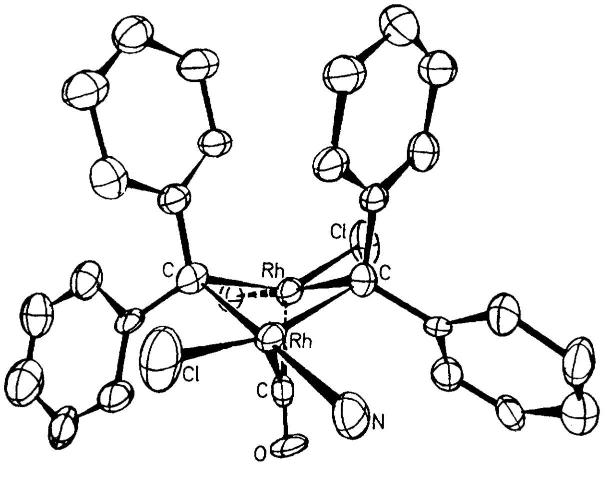
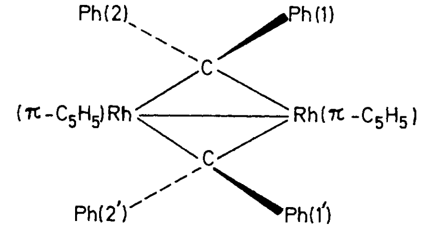


FIGURE. An ORTEP drawing of $[Rh(CPh_2)Cl(C_5H_5N)]_2CO$. Only the nitrogen atoms of the pyridine rings are included for clarity.



The Rh–Rh distance of 2·51 Å is comparable to the value of 2·63, 2·66, and 2·69 Å found in $[(Ph_3P)_2Rh(CO)]_2,2CH_2Cl_2$,[4] $(C_5H_5)_3Rh_3(CO)_3$,[5] and Rh metal[6] respectively and indicates the existence of a rhodium–rhodium bond. The atom arrangement about the bridging carbene carbon is very similar to that found in 1,1-diphenylcyclopropane derivatives.[7]

The carbene and carbonyl resonances of compound (III) also appear as sharp triplets at room temperature and −90°. The carbonyl chemical shift and $J(^{103}Rh\text{-}^{13}C)$ values are those expected for a bridging carbonyl. Thus we propose that (III) has a triple bridging structure analogous to (II).[8] The ^{13}C n.m.r. signal for the carbene carbons of (IV) is a triplet suggesting that these two ligands are also in bridging

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† Compound (II) was previously formulated as $[Rh(CPh_2)Cl(C_5H_5N)CO]_2$ (see ref. 1). Our single-crystal *X*-ray results (*vide infra*) clearly show that this formula is incorrect.

positions. The appearance of seven resonances in the phenyl region of the ^{13}C n.m.r. spectrum of (III) indicates that the two phenyl groups attached to the carbene carbon are not equivalent in this complex. However for (IV) only four resonances for the phenyl groups were observed suggesting increased symmetry for this complex. Based on this information, we propose the following structure for (IV) in solution.[8]

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