Inorganica Chimica Acta, 53 (1981) L223–L224

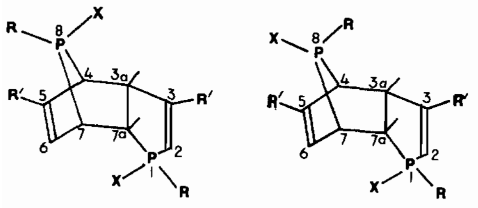
Retention of Stereospecific ^{31}P Chemical Shift and Coupling Phenomena in a Heterocyclic Diphosphine upon Complexation with a Cobaloxime

LOUIS D. QUIN*, KEITH A. MESCH, FRANCES STONEBERGER PINAULT and ALVIN L. CRUMBLISS*

P. M. Gross Chemical Laboratory, Duke University, Durham, N.C. 27706, U.S.A.

Received January 26, 1981

The recently synthesized [1, 2] series of novel diphosphine ligands 1–4 (formally dimers of phospholes) are capable of bonding to two transition metal centers through the lone pairs of electrons on the P atoms. In initiating studies on the coordination chemistry of these ligands, we have used methylcobaloxime, $Co(dmgH)_2(CH_3)$**, as the metal complex moiety due to the ease with which it forms ligand-bridged binuclear complexes [3], and its demonstrated utility in NMR investigations [4]. These coordinated phosphines exhibit novel NMR phenomena of a type previously unreported for a phosphine complexed to a metal. Several stereospecific NMR features found in the phosphine ligands 1–4 were retained in the corresponding dicobaloxime complexes 5–8. This observation is of special significance since the features of stereospecificity, to be described in this report, are not reproduced in P(IV) derivatives of the phosphines such as oxides, sulfides, and quaternary salts and are generally thought to be peculiar to the P(III) state.



R=CH₃, R′=H, X=lone pair	1	2
R=R′=CH₃, X=lone pair	3	4
R=CH₃, R′=H, X=Co(dmgH)₂(CH₃)	5	6
R=R′=CH₃, X=Co(dmgH)₂(CH₃)	7	8

TABLE I. ^{31}P NMR Data.

Ligand	Complex	δ ^{31}P^{a}		$^{3}J_{PP}$ (Hz)
		P$_8$	P$_1$	
1		+96.5	−2.3	24.4
	5	+135.1	+38.0	34.2
2		+30.2	−7.9	0
	6	+89.7	+32.4	0
3		+100.7	−1.9	24.4
	7	+136.4	+37.1	34.2
4		+27.3	−8.7	0
	8	+83.5	+32.0	0

^{a}Fourier transform, proton-decoupled; positive shifts are downfield, negative upfield, of 85% H_3PO_4 as reference.

These stable diphosphine bridged dicobaloximes† are synthesized from $Co(dmgH)_2(CH_3)(S(CH_3)_2)$ and the diphosphine in chloroform. ^{1}H NMR spectroscopy confirmed that dicobaloxime formation occurred via coordination at the P atom lone pair of electrons, since P–H coupling (J_{P-H} = 3.7–4.4 Hz) of the axial Co–CH_3 protons was observed in both cobaloxime moieties.

One of the unique properties of these diphosphines is the totally different ^{31}P NMR spectra exhibited by a pair of *syn* (1, 3) and *anti* (2, 4) isomers. The bridging P is extraordinarily deshielded in the *syn* isomers, and only moderately deshielded in the *anti* [1, 2]. Also three-bond ^{31}P–^{31}P coupling is strong (24.4 Hz) in the *syn* and totally absent in the *anti* series. These effects are reproduced exactly in the dicobaloxime complexes. While both P nuclei exhibit downfield coordination shifts of 35–60 ppm (Table I), the large difference between them is maintained. Equally significant is the observation that the *syn* ligand retains large (34.2 Hz) P–P coupling and the *anti* isomer again is seen to exhibit ***no coupling*** in spite of the fact that the geometrical disposition of these nuclei is the same in both isomers. Conversion of the diphosphines to oxides, sulfides, or salts, on the other hand, is known [5] to cause collapse of this coupling difference.

Remarkable also is the retention of stereospecific two-bond and three-bond couplings to ^{13}C in the complexes. $^{2}J_{PC}$ is known to be large in phosphines when the lone pair is in close proximity to the coupled carbon [6] and small (even absent) when remote. This is clearly evident in the phosphole dimers (Table II). Thus in the *syn* compounds, coupling due to P-8

---

*Author to whom correspondence should be addressed.

**dmgH = the dimethylglyoximato monoanion, $[CH_3C(=NOH)C(=NO)CH_3]^-$.

†Satisfactory elemental analyses were obtained.

TABLE II. Partial ^{13}C NMR Data.[a]

Compound	C-3	C-3a	C-5	C-6	C-7a
3	151.2(10.4)	59.6(28.1)	142.3(4.8)	125.8(4.8)	48.8(23.9)
4	152.0(0)	60.3(3.8)	144.6(19.4)	127.4(19.5)	47.5(1.8)
7	156.8(7.9)	56.8(19.7)	143.4(0)	129.1(0)	42.3(18.0)
8	155.5(0)	59.5(0)	139.8(13.8)	126.3(5.9)	43.9(0)

[a] Chemical shifts expressed in ppm downfield form TMS using the center peak of $CDCl_3$ (76.9 ppm) as the calibrant. Values in parentheses are $^{31}P-^{13}C$ coupling constants for ^{31}P-8 to ^{13}C, in Hz.

is small to C-5 and C-6 (*e.g.*, both 4.8 Hz in 3) and large to C-3a and 7a (28.1 and 23.9 Hz, respectively), while in the *anti* series the reverse is observed. These relations are present also in the dicobaloxime complexes. Similarly, $^3J_{PC}$ is known to be controlled by the configuration of P(III) [7], and in the free diphosphines this is seen by examining coupling to C-3 from the bridging P (*syn*, 10.4 Hz in 3; *anti*, 0 Hz in 4). In the complexes of these phosphines, coupling is 7.9 and 0 Hz, respectively. These stereospecificities vanish in oxides, sulfides, and salt [8].

No theoretical explanations for the control of $^2J_{PC}$ and $^3J_{PC}$ by configurational differences at phosphines in rigid systems have yet been published, nor has an explanation been developed for the truly remarkable deshielding at the bridging P in the phosphole dimers. Our new results make an important contribution to these matters; the non-bonded phosphorus lone pair of the free phosphines *per se* cannot be directly responsible for either the coupling or the shift effects, since this lone pair is involved in sigma bond formation to cobalt in the dicobaloxime complexes. A satisfactory explanation for the common NMR characteristics of phosphorus in both free and complexed form has yet to be developed.

Acknowledgements

Financial support from NIH-BRSG (A. L. C. and L. D. Q.), Research Corporation (A. L. C.) and a NATO collaborative research grant (A. L. C.) which enabled discussion with Professor A. Gaudemer, University of Paris-Orsay, is gratefully acknowledged.

References

1 L. D. Quin and K. A. Mesch, *J. Chem. Soc. Chem. Comm.*, 959 (1980).
2 K. A. Mesch and L. D. Quin, *Tetrahedron Letters*, in press.
3 D. Dodd and M. D. Johnson, *J. Chem. Soc. Dalton*, 1218 (1973); P. L. Gaus and A. L. Crumbliss, *Inorg. Chem., 15,* 2080 (1976); J. M. Ciskowski and A. L. Crumbliss, *Inorg. Chem., 18,* 638 (1979).
4 See for example: C. Bied-Charreton, L. Alais and A. Gaudemer, *Bull. Soc. Chim. Fr.*, 861 (1972); C. Bied-Charreton, A. Gaudemer, C. A. Chapman, D. Dodd, B. D. Gupta, M. D. Johnson, B. L. Lockman and B. Septe, *J. Chem. Soc. Dalton*, 1807 (1978); J. A. Kargol, R. W. Crecely, J. L. Burmeister, P. J. Tascano and L. G. Marzilli, *Inorg. Chim. Acta, 40,* 79 (1980) and references therein.
5 L. D. Quin and K. A. Mesch, *Org. Magn. Resonance, 12,* 442 (1979).
G. A. Gray and S. E. Cremer, *J. Chem. Soc. Chem. Comm.*, 367 (1972); J. J. Breen, S. I. Featherman, L. D. Quin and R. C. Stocks, *J. Chem. Soc. Chem. Comm.*, 657 (1972);
6 L. D. Quin, M. J. Gallagher, G. T. Cunkle and D. B. Chesnut, *J. Am. Chem. Soc., 102,* 3136 (1980).
7 S. Sorensen and H. J. Jakobsen, *Org. Magn. Resonance, 9,* 101 (1977).
8 L. D. Quin and K. A. Mesch, unpublished results.