



COORDINATION COMPLEXES OF PALLADIUM DICHLORIDE WITH 4-SUBSTITUTED NITROBENZENES

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(Received 13 December 1994; accepted 20 December 1994)

Abstract—Complexes of 4-substituted nitrosobenzenes with palladium dichloride have been prepared and studied by solid state CP/MAS ^{13}C NMR spectroscopy. The results obtained are discussed in terms of the unique property of the nitroso group based upon its high π -electron accepting character. It is shown that this property is maintained when the NO group undergoes σ_{N} coordination to palladium in contrast to recent evidence that π_{NO} coordination to molybdenum removes this property. The effect of coordination upon the chemical shifts of the other ring carbons is also discussed.

Bis(nitrosobenzene) palladium dichloride was first prepared in 1969¹ and the X-ray crystal structure determination clearly demonstrated that the coordination was σ_{N} and that the two nitrosobenzene units were equivalent.² To the best of our knowledge preparation of the analogous 4-substituted nitrosobenzene coordination complexes of palladium dichloride has not been attempted apart from the dimethylamino substituent.³ We have shown⁴ that the NO group in 4-substituted nitrosobenzenes possesses a unique feature as demonstrated by ^{13}C NMR spectroscopy in that the resonance of C-NO occurs at a higher value in the unsubstituted compound than for any 4-substituted compound. Such behaviour is not found for at least 35 other functional groups (X) where the presence

of π -acceptor groups in the 4-position leads to C-X resonances at higher values than in the unsubstituted compound. This unusual behaviour is ascribed⁴⁻⁶ to the high π -electron acceptor character of the NO group which effectively converts the π -electron acceptor groups in the 4-position into π -electron donors. We have used solid state ^{13}C NMR spectroscopy⁷⁻¹⁰ to obtain information on the structure of the ligand in a variety of coordination complexes of C-nitrosocompounds. It is possible to add to this understanding by carrying out similar studies for the palladium dichloride complexes and also to establish whether the unique property of the NO group shown by ^{13}C NMR spectroscopy⁴ survives in complexes of 4-substituted nitrosobenzenes where the NO is σ_{N} coordinated to a metal.

EXPERIMENTAL

The coordination compounds $(4\text{-X-C}_6\text{H}_4\text{NO})_2\text{PdCl}_2$ were prepared by the method of Balch and Petridis,¹ i.e. by reaction of a methylene chloride solution of the nitrosobenzene with a methylene

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chloride solution of bis(benzonitrile) palladium dichloride. In all cases the solids were blue-black in colour. IR spectra were measured in Nujol except where noted.

X = H. Details as in literature,¹ IR (cm⁻¹, KBr) 3050w, 1583s, 1499vs, 1458m, 1437s, 1342m, 1305m, 1195s, 1183m, 1127vs, 996m, 880s, 837w, 778s, 684s, 663s, 626s.

X = F. M.p. 140–3, formula requires C 33.7, H 1.9, N 6.6%. Found: C 32.4, H 1.9, N 6.2%, IR (cm⁻¹) 1590s, 1500s, 1245s, 1178m, 1125vs, 895m, 850m, 765m.

X = NO₂. M.p. 165–8, formula requires C 29.9, H 1.7, N 11.6%. Found: C 30.5, H 1.7, N 11.9%. IR (cm⁻¹) 1590s, 1518b,vs, 1340b,vs, 1330s, 1171m, 1122s, 1110m, 1005m, 860s, 840m, 750m.

X = OCH₃. M.p. 242 dec., formula requires C 37.2, H 3.1, N 5.1%. Found: C 37.3, H 3.0, N 6.4%. IR (cm⁻¹) 1591vs, 1560m, 1500s, 1348s, 1290vs, 1222vs, 1185m, 1145b,vs, 1112s, 999s, 890m, 859s, 785m, 730m.

X = CH₃. M.p. 191–4, formula requires C 40.1, H 3.4, N 6.7%. Found: C 39.3, H 3.4, N 6.7%. IR (cm⁻¹) 1592s, 1500s, 1330m, 1300m, 1202s, 1140b,vs, 1030m, 990m, 885s, 830s, 780m.

X = CO₂CH₃. M.p. > 200, formula requires C 37.9, H 2.8, N 5.5%. Found: C 37.9, H 2.7, N 5.6%. IR (cm⁻¹) 1715b,vs, 1598m, 1518s, 1512s, 1281b,s, 1175s, 1135vs, 1110vs, 1003m, 952s, 885s, 875s, 820s, 771s, 709m, 680s, 621s.

The solid state CP MAS ¹³C NMR spectra for the above complexes and for X = H and N(CH₃)₂ are given in Table 1. These were obtained at the University of Durham Industrial Research Laboratories using the following operating conditions. 75.431 MHz, contact times ranged from 1.0 to 5.0 ms, relaxation delays from 2.0 to 60.0 s, MAS rates from 3480 to 4970 Hz. All cross-polarization spectra were obtained with the Hartman–Hahn match condition fulfilled. The carbon secondary reference

standard was the adamantane CH₂ signal at 38.4 ppm relative to TMS.

RESULTS AND DISCUSSION

The parent compound, dichloro(bisnitrosobenzene)palladium(II), is of fundamental importance for the interpretation of the NMR data because its crystal structure has been determined² and it is clearly established that the monomeric nitrosobenzene ligands are coordinated solely through the nitrogen atom. The phenyl ring is twisted by 11.8° from the C(phenyl)—N—O plane and the CNO angle at 118.2° is larger than that usually found in monomeric C-nitroso compounds, see e.g. ethyl-*m*-nitroso-*trans*-cinnamate 113.5°¹¹ and *p*-nitrosoanisole 113.6°.¹² It is important to compare the chemical shifts for the coordinated nitrosobenzene with those for nitrosobenzene in solution.⁴ All of the chemical shifts are increased to a higher value on coordination, C1 by 0.9 ppm, C4 by 9.2 ppm, the C2,6 average by 8.8 ppm, and the C3,5 average by 1.5 ppm. The greatest effect therefore is to be found in the carbon atom most remote from the coordinating NO group.

Reference to Table 1 clearly establishes that the shifts of the C1 carbons in the complexes (4-X-C₆H₄-NO)₂PdCl₂ are all at lower values than that for X = H where the X group is a π-electron donor. This behaviour is as expected for such groups. When X is the π-electron acceptor CO₂CH₃, the C1 shift occurs at a marginally lower value than for X = H. When X = NO₂, there is a very small increase in the C1 shift compared to that in the unsubstituted complex but it is also apparent that the C2,6 shifts are the same in contrast to all of the other cases studied. This equivalence of the 2 and 6 carbons suggests either that the coordinated NO group is orthogonal to the plane of the ring or that this group can undergo free rotation in the solid at

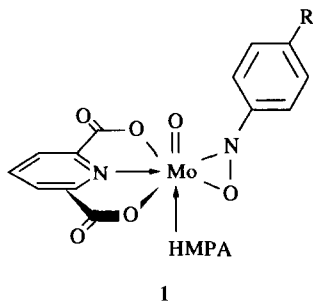
Table 1. ¹³C NMR Spectra of complexes (4-XC₆H₄NO)₂PdCl₂ (values in ppm)

X	C(1) ^a	C(2)	C(3)	C(4)	C(5)	C(6)	Other
H	167.0	117.7	131.7	144.7	130.1	141.7	
Me	166.6	115.9	132.4	157.7	132.4	141.6	25.7
OMe	161.6	118.1	114.6	171.1	123.3	145.2	60.2
F	165.2	110.4	120.4	169.5	120.4	144.9	
NO ₂	167.7	129.2	124.1	164.6	124.1	129.2	
CO ₂ Me	166.8	117.2	132.4	139.3	132.4	141.5	164.8, 54.1

^a The carbon attached to the NO group is numbered (1); the carbon syn to the O of the NO group is numbered (2). Where the C(3) and C(5) shifts are not identical it is possible that the assignments may be interchanged.

room temperature: either of these would thereby remove the effect of the magnetic anisotropy of the NO group upon the C2 and 6 carbons. We have shown elsewhere¹³ that the C1 shift rises and the C2 and 6 shifts are identical when the NO group is situated orthogonal to the plane of the benzene ring as in 2, 4, 6-tri-*tert*-butylnitrosobenzene. This slight rise of the C1 shift from 167.0 (X = H) to 167.7 ppm (X = NO₂) could thus be due to orthogonality rather than the breakdown of the extreme π -electron attracting power of the NO group on σ_N coordination.

The crystal structure of the nitrosobenzene complex² shows that the NO group is only slightly displaced from the in plane *anti* position, and it is expected that this is repeated for all the 4-substituted nitrosobenzene ligands with the exception of the nitro substituent. It is well established that when the NO group is fixed in plane with the ring that its large magnetic anisotropy leads to the largest splitting of the C2 and C6 resonances that has been yet discovered for any functional group¹⁴ and that this magnetic anisotropic effect can persist with only slight diminution when the NO group of *p*-nitrosoanilines is coordinated to metals.⁸⁻¹⁰ With the exception of the nitro substituent we have large splittings of the C2 and 6 shifts ($\Delta_{2,6}$ in the range -24 to -34.5 ppm) and these values are comparable with those which we have observed^{8,9} for σ_N and σ_O complexes of 4-dimethylaminonitrosobenzene. It is therefore concluded that when the σ coordination of a nitrosobenzene to a metal occurs, accompanied by only minor changes in twisting of the NO group from coplanarity with the ring, then the coordinated NO group retains a substantial degree of the magnetic anisotropy that can be shown to be present in the NO of the uncoordinated ligand in which free rotation has been prevented either by carrying out the measurements on solid monomeric nitrosocompounds or by the "freezing out" of the rotation at low temperatures.



When our initial studies of the ¹³C NMR spectroscopy of 4-substituted nitrosobenzenes were

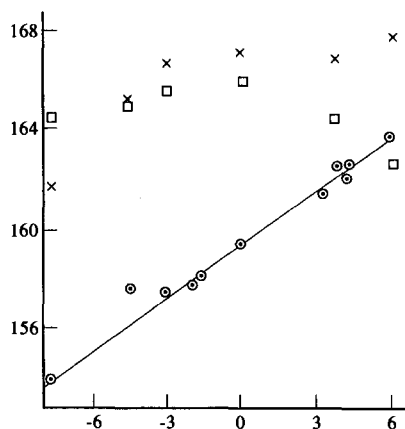


Fig. 1. Values of C(1) of the 4-substituted nitrosobenzene of the π_{NO} molybdenum complex **1** (⊙) plotted against the *para*-Substituent Chemical Shifts¹⁷ of C₆H₅X compared with those obtained for (4-XC₆H₄NO)₂PdCl₂ (×) and for 4-XC₆H₄NO⁴ (□).

made and the unusual results ascribed⁴ to the extremely high electron demand of the NO group, no data were available to indicate whether this property was maintained for coordinated nitrosobenzenes. The recent results of Møller and Jørgensen¹⁵ for nitrosobenzenes π coordinated to molybdenum (VI), which are displayed in Fig. 1, clearly demonstrate that the π coordinated NO group behaves in the same manner as all other functional groups and does not have the unusual property associated with NO itself. On the other hand, our results for nitrosobenzenes σ_N coordinated to palladium when compared with the same nitrosobenzenes themselves suggest that there is some slight modification of the high electron demand of the NO group following upon σ_N coordination but that the unusual property revealed by ¹³C NMR spectroscopy is maintained. This property of the NO group may also be linked to the fact that the O-atoms of C-nitrosocompounds are the most deshielded by far of the O-containing functional groups.¹⁶ The slope of the continuous line (0.70) in Fig. 1 is similar to those observed by Lynch¹⁸ for the amino group (0.83), the methoxy group (0.71) and the nitro group (0.82).

Acknowledgements—M.C. thanks the SERC for a research studentship. B.G.G. thanks the Leverhulme Trust for the award of an Emeritus Fellowship and the SERC for an allocation of solid state NMR spectra measured at the University of Durham, and Professor R. K. Harris and Dr D. C. Apperley for the spectra obtained and discussion thereof.

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