ESRF	Experiment title: Electron density deformation studies on new allenylidene complexes	Experiment number: CH-487
Beamline: ID 11	Date of experiment: from: 27/08/98 to: 31/08/98	Date of report: 26/2/99
Shifts: 12	Local contact(s): Kvick Ake	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

* Carole Ménoret, SPMS, UMR 8850 CNRS, Ecole Centrale Paris, 92295 Châtenay-Malabry
* Anne Spasojevic
* Gianguido Baldinozzi

Mohamed Souhassou , Laboratoire LCM3B, UPRESA 7036 du CNRS, Nancy I, BP 239, 54506 Vandoeuvre-les-Nancy Cedex

Helmut Fischer, Fakultät für Chemie, Universität Konstanz, Postfach 5560 M727, D-78434 Konstanz, Germany

Mickael Hopkins, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa 15260

The aim of this experiment was to study in more details the behaviour of the allenylidene complexes by electron density deformation. We wanted to observe the slight modifications in the chemical bonds due to the different substituents by performing several charge density studies on compounds of the same series. Unfortunately, because of the poor crystalline quality of our allenylidene single crystals, we were not able to perform an experiment with these complexes. Therefore, we have undertaken the study of two compounds: the cumulene ($CO_5WNCN(C_2H_5)_2$, (WDEC) and the carbyne ($BrWCH(dmpe)_2$, (WCARB) complexes.

For the former one, we wanted to prove the feasibility of a charge density deformation study with a heavy metal atom (5d). To obtain the best experimental conditions the data collection was performed with a CCD camera on ID 11 at ESRF. Valuable information was obtained by comparing to the isomorphous compound ($CO_5CrNCN(C_2H_5)_2$, (CrDEC) [1]. For the latter one, a very original compound possessing a rare W ≡ C – H group, classical crystallographic studies using a Mo source have been undertaken but the dmpe configuration ($Me_2PCH_2CH_2PMe_2$), the position of H atoms, ... were not very accurate [2].

Single crystals were glued to glass fibers and inserted into brass pins. All the manipulations were performed under inert atmosphere. Diffraction data were collected on ID11 3-circles diffractometer equipped with a CCD camera. A short wavelength (λ = 0.4747Å) was the best compromise between highest flux and minimum absorption due to W atoms. Single crystals were kept at 123 K in a nitrogen cryostream flux (Oxford Instruments). The integrated intensities were extracted using SAINT [3]. Since WDEC was slightly twinned, special attention was paid for the choice of integration boxes. A successful integration was obtained by optimizing the orientation matrix and the size of the integrated box for each series of frames and, when necessary, for single parts of a series. The extraction of integrated intensities was carried out without no particular problem for the other compound. In both cases the absorption and the decay were corrected by SADABS [4]. Full matrix least-square refinements were performed using SHELX97 [5] and JANA [6] packages (table). All the hydrogen atoms were successfully located and the average bond lengths C-H are very satisfying $<(d_{C\text{-}H} = 1.01(9)$ Å$)_{WDEC}>$.

Concerning the WCARB structure (fig. 1), the specific behaviour of the dmpe ligand observed for a series of L-W (≡CH) $(dmpe)_2$ [2] (L= Cl, Br, n-Bu, . . .) has also been determined for WCARB in a more accurate way. The three $C_{carbyne}$ – W – P angles are about <92.06(11)°> and they are in agreement with the σ-donor / π-acceptor character of the *trans* ligand. On the other hand, the fourth angle, unexpectedly, exhibits a different value 96.46(11)°. Moreover, the disordered character of one of the two dmpe can be expressed by the ratio $<Ueq, C_{disordered\ dpme}>$ / $<Ueq, C_{ordered\ dmpe}>$. This ratio (1.33) compares favorably to those obtained by single crystal neutron diffraction at 100 K (1.32) and at room temperature (1.48) [7]. We have been able to explain these results by an accurate quantitative

examination of the packing arrangement. In order to minimize the unfavorable Van der Waals interaction between the two methyl groups in the dmpe ligands in adjacent molecules, one of the P atoms is kicked out of the equatorial plane while the C atoms of the other dmpe sit alternatively on two different positions.

For the WDEC structure (fig. 2), we have already begun to undertake the multipolar refinement. Due to the difficulty of an exact estimation of the form factor of W, we have used, in a preliminary phase of the refinement, the multipole parameters obtained from the isomorphous compound CrDEC (fig. 3).

ESRF- ID11 beam-line	WDEC, cumulene	WCARB, carbyne
Formula	$C_{10}H_{14}WN_2O_5$	$BrWP_4C_{13}H_{33}$
Main bonds	OCW=N=C=N	BrW≡CH
Space group, Z	C2/c, 4	$P2_1/n$, 4
a, b, c (Å)	13.600(1), 11.602(2), 9.364(1)	9.1061(1), 18.4250(2), 12.7516(2)
β (°), volume (Å^3)	116.052(1), 1327.40(5)	100.688(3), 2102.34(6)
μ (mm^{-1}), F(000), T (K)	1.36, 792, 123	1.38, 1120, 123
Crystal dimensions (mm)	0.31 x 0.35 x 0.39	0.13 x 0.16 x 0.22
2θ detector (°), scan mode, width (°)	30, ϕ scan, ω scan, 0.1	30, ϕ scan, ω scan, 0.1
$\sin(\theta/\lambda)_{max}$ (Å^{-1}), time per frame (s)	1.03, 1.6	1.03, 1.6
Number of frames recorded	12705	8954
Reference frames	100 frames every 27 min	100 frames every 27 min
Size of the integrated box (Å. °)	2.6 x 2.6 x 2.85 (averaged)	1.4 x 1.4 x 1.6
Measured, independent, (I>3σ) refl.	35716, 5606, 5394	75685, 18036, 15338
$R_{int}(F^2)$ before, after Sadabs	0.061, 0.032	0.099, 0.0395
Number of parameters, $R_1(F)$, G.O.F	85, 0.035, 1.148	172, 0.0454, 1.12

Figure 1. Molecular structure of WCARB

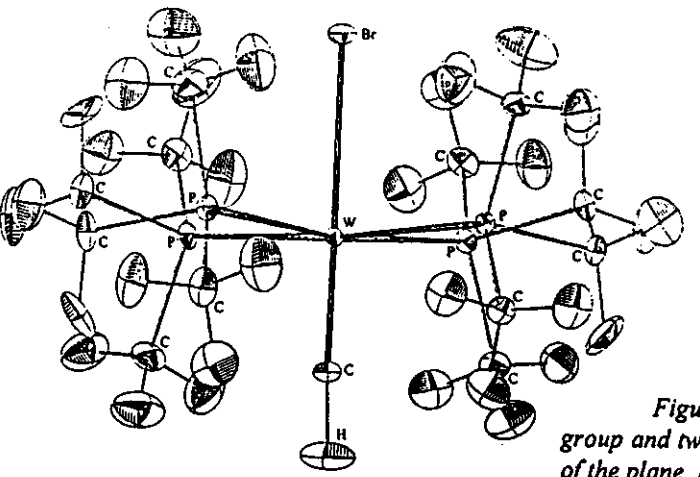


Figure 2. Molecular structure of WDEC

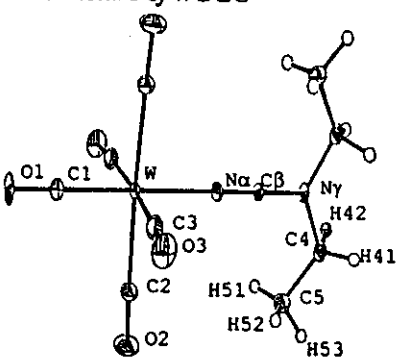
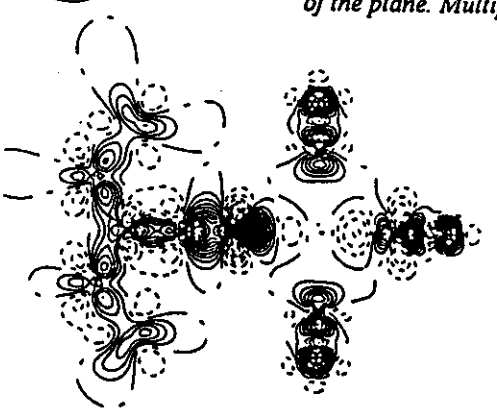
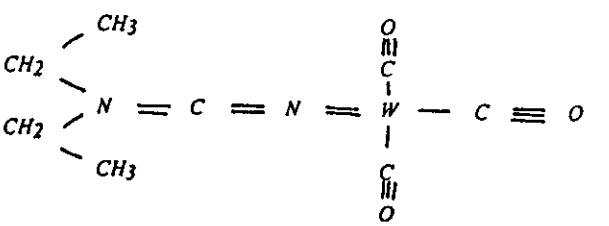


Figure 3. Static map of WDEC in the plane containing the OCWNCN group and two CO groups. The diethyl groups and the cis-oxygen are slightly out of the plane. Multipole parameters obtained from CrDEC [1]. Contours 0.1 e.Å^{-3}.





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