The purity was controlled with 0.25 mm silica gel thin-layer chromatograms with dichloromethane, ethyl ether, and hexane 2:3:4 as moving solvent. The R_F-values were 0.23 for DMNA and 0.48 for DENA.

The work with DMNA and DENA must be carried out with the greatest caution. These compounds are extremely potent carcinogens [1,4] even in very low concentrations. They seem to be a major candidate class of carcinogens that are likely to be causally related to human cancer.[4]

DMNA and DENA are dissolved in liquid, pure cetyl alcohol at 50°. Thin layers, suitable for reflection spectrophotometry are easily prepared by shedding the solution on frosted quartz plates at the same temperature. Depending on the construction of the spectrophotometer used, areas from 5 mm² upwards can be measured. Spectroreflectometers with an integrating sphere, as used in the measurement of the contribution of fluorescence to the brightness of papers treated with whitening agents,[5] allow a convenient work but require a reflecting area of approximately 315 mm². A suitable layer thickness which always should be kept constant, is 0.2 mm, corresponding to 0.162 mg cetyl alcohol/mm² at 20°, or 51 mg cetyl alcohol on the larger area of 315 mm² of spectroreflectometers with integrating sphere. The measurements reported in this paper were carried out with integrating sphere, using 60 mg cetyl alcohol on 315 mm². The appropriate quantity of cetyl alcohol, and solution of N-nitrosodialkylamines in cetyl alcohol, respectively, was applied with an automatic pipette.

A 5″ strip chart linear and log potentiometric recorder was used.

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On Some Kinematic Phenomena in π-Benzene Sandwich Compounds

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In a recent work we have performed [1] a vibrational analysis of dibenzenechromium, $Cr(C_6H_6)_2$, treated as a 25 atomic molecule. In contrast to former partial analyses [2] the study revealed an interesting kinematic coupling between some ligand and framework normal vibrations. The most striking manifestation of this coupling was observed for the A_{2u} non-planar C—H deformation of benzene. Its frequency is found at 794 cm⁻¹ (IR, in-phase, A_{2u}) [4,5] and at 791 cm⁻¹ (Raman, out-of-phase, A_{1g}) [2] in the spectra of dibenzenechromium (DBC). Its value in free benzene is much lower (671 cm⁻¹).[6] Consequently, the corresponding force constant for DBC is increased very much (39.7 %) [2] over the free benzene value, if a normal coordinate analysis is executed treating benzene in DBC as an isolated molecule with D_{6h} symmetry.

In marked contrast a total vibrational analysis of DBC as a 25 atomic complex allows a reproduction of the observed A_{2u} frequency by a force constant which is exactly the same as that of free benzene.[1] This astonishing fact is caused by a strong coupling between No. 11 (A_{2u}) [4] and Nos. 23 (A_{2u}) and 21 (A_{1g}) [3,4] in the IR and the Raman spectra, respectively. The reason for this coupling is a nonvanishing off-diagonal element in the corresponding G-matrix block.

In order to check whether the same coupling is also found in other benzene sandwiches, we have executed a total normal coordinate analysis of $Cr(C_6H_6)_2{}^+$, $V(C_6H_6)_2$, $Mo(C_6H_6)_2$, $W(C_6H_6)_2$, $Tc(C_6H_6)_2{}^+$ and $Re(C_6H_6)_2{}^+$, using without any additional refinement the same force field and the same structural parameters as in the DBC study.[1] The result for the No. 11 A_{2u}

Table 1. Experimental [3,4,5,7] and calculated frequencies in cm^{-1} of the normal modes Nos. 11 (A_{2u}), 23 (A_{2u}) and 25 (E_{1u}) of various sandwich compounds and benzene. In all the cases the unchanged force field of dibenzenechromium [1] was used.

Frequency No.	11		25		23	
	obs.	calc.	obs.	calc.	obs.	calc.
$Cr(C_6H_6)_2$	794	794	459	459	490	490
$Cr(C_6H_6)_2^+$	795	794	415	459	466	490
$V(C_6H_6)_2$	742	796	429	463	478	493
$Mo(C_6H_6)_2$	773	760	362	372	424	415
$Mo(C_6H_6)_2^+$	—	760	333	372	410	415
$W(C_6H_6)_2$	798	745	331	313	386	355
$W(C_6H_6)_2^+$	—	745	306	313	378	355
$Tc(C_6H_6)_2^+$	—	759	358	369	431	411
$Re(C_6H_6)_2^+$	—	745	336	312	396	354
C_6H_6	671	671	—	—	—	—

mode is shown in Table 1 and compared with the experimental values. In all the inspected cases the observed frequencies are higher than in free benzene.[4] In good qualitative agreement all the observed frequency shifts can be reproduced by the unchanged free benzene force constant due to the mentioned kinematic coupling.

An additional interesting kinematic effect is found for this series and the IR active Nos. 23 and 25 metal-ligand vibrations. In the individual compounds these frequencies can vary considerably [3,4,7] (Table 1). If, in the vibrational analysis of these complexes, all parameters are kept constant (referred to DBC) and the only change allowed is that for the mass of the central atom, then one observes the interesting phenomenon that the qualitative appearance of this series of frequencies is well reproduced (Table 1). All calculated frequencies are shifted in the direction of the observed values. This seems to reveal the astonishing fact that in the investigated benzene sandwiches these metal-ligand vibrations are less influenced by the electronic configuration of the central atom as one might expect (note the small differences for V, Cr, and Cr^+) than they are influenced by the mass of the complexed atom (note the large differences for Cr, W, and Mo).

Consequently, the bonding force between benzene and the central atom in these compounds is much less influenced by the electronic configuration of the central atom, than the qualitative inspection of the vibrational spectrum would suggest. This is somewhat in contrast to qualitative considerations,[8] on the basis of which it was claimed that benzene in such sandwich compounds is distorted from six-fold to three-fold symmetry, when the electronic configuration of the central atom changes from $3d^5$ to $3d^6$.

A more detailed analysis of these molecules may be performed when more structural and spectroscopic data are available.

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