to zero via spin-lattice relaxation. The initial buildup rates of the NOE’s depend only on the cross relaxation coefficients between the irradiated spin and the observed nuclei, and are thus directly related to the inverse of the sixth power of the proton-proton distances in the three-dimensional structure of the protein.

The following are some details to be observed in the transient NOE's of Figures 2 and 3. At \( \tau = 0 \), the line corresponding to the geminal methylene proton with respect to the pulsed nucleus has already emerged because of spin diffusion during the 15 ms of the pulse duration. In Figure 3 the additional appearance of the methyl signal at \( \tau = 0 \) trace is a trivial consequence of the limited selectivity of the inversion pulse applied to the line \( \gamma \). In both Figures 2 and 3 a line at 3.1 ppm grows at about the same rate as the \( \beta \)-methylene signals of Met 80. From two decoupled NOE difference spectra, where, respectively, the \( \beta \) or \( \beta' \) line was irradiated for spin pumping prior to spin decoupling during data acquisition,\(^7\) this resonance was independently assigned to the \( \alpha \)-proton line of Met 80. It is seen that the \( \alpha \)-proton resonance grows faster when the \( \gamma \) peak is pulsed than when the \( \gamma \) peak is pulsed. In Figure 3 the \( \alpha \)-proton resonance has already appeared at \( \tau = 25 \) ms, whereas it has not emerged until 50 ms in Figure 2. Corresponding transient NOE’s were obtained after application of selective inversion pulses to the resonances \( \beta \) and \( \beta' \) (Figure 1). It was found that the \( \alpha \)-proton line of Met 80 grows faster after irradiation of resonance \( \beta' \) than after irradiation of \( \beta \). In an additional experiment the resonances \( \gamma \) and \( \gamma' \) were found to grow faster than \( \beta \) and \( \beta' \) after pulse inversion of the Met 80 methyl line \( \epsilon \).

From these experiments the increased information content of transient NOE studies in macromolecules (Figures 2 and 3) as compared to the more conventional steady-state experiments (Figure 1) is readily apparent. While the steady-state NOE was able to distinguish between the \( \beta \)- and \( \gamma \)-methylene protons, the transient NOE’s further distinguished between \( \beta \) and \( \beta' \) and \( \gamma \) and \( \gamma' \), respectively, of the axial Met 80. These assignments agree with those generally accepted,\(^6\) which were originally suggested from ring-current calculations based on the X-ray structure.\(^3\) The transient NOE’s provided further information on static and dynamic aspects of the spatial arrangement of Met 80 in the protein. The different growth rates of the \( \alpha \)-proton line (Figures 2 and 3) clearly show that the protons \( \beta \) and \( \gamma \) are located more closely to the \( \alpha \) proton than the protons \( \beta' \) and \( \gamma' \). Since they are at higher field (Figure I), the \( \beta' \) and \( \gamma' \) protons must also be closest to the plane of the ring.

That the different local environments of the individual \( \beta \)- and \( \gamma \)-methylene protons are manifested in the transient NOE’s further shows that the rotational mobility about the single bonds in the side chain of Met 80 is severely limited in ferrocychrome \( \epsilon \). Finally, experiments of the type of Figures 2 and 3 provide a convincing demonstration of spin diffusion pathways in proteins. Overall, the present experiments imply that spin diffusion in macromolecules, rather than leading necessarily to less specific and hence less useful NOE’s,\(^7\) may through suitable use of the two-dimensional frequency-time space of transient NOE experiments lead to novel insights into the molecular structures which might not be available otherwise.

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References and Notes

(11) Experiments of the type discussed in this communication were alluded to in the closing paragraph of ref 2. Transient NOE experiments on small molecules have been carried out frequently, for example, Freeman, R.; Hill, H. D. W.; Tomlinson, B. L. J. Chem. Phys. 1974, 61, 4466–4473. As in the earlier work, it was found that the enhanced NOE signal was temperature-dependent. It was found that the a-proton line of Met 80 grows faster after pulse inversion of the Met 80 methyl line than after irradiation of the y peak is pulsed. In Figure 3 the a-proton resonance has already appeared at \( \tau = 25 \) ms, whereas it has not emerged until 50 ms in Figure 2. Corresponding transient NOE’s were obtained after application of selective inversion pulses to the resonances \( \beta \) and \( \beta' \) (Figure 1). It was found that the a-proton line of Met 80 grows faster after irradiation of resonance \( \beta' \) than after irradiation of \( \beta \). In an additional experiment the resonances \( \gamma \) and \( \gamma' \) were found to grow faster than \( \beta \) and \( \beta' \) after pulse inversion of the Met 80 methyl line \( \epsilon \).

We have already reported the isolation and characterization of two members of a family of rhodium carbonyl cluster anions, [Rhl2(CO)12][H5glycine]((2, n = 2, 3), containing a metal atom polyhedron which is part of a hexagonal close-packed lattice.\(^1\) These have been studied by X-ray diffraction\(^4\) and by NMR spectroscopy.\(^3\) We report here the characterization of two new high nuclearity rhodium clusters which show different types of metal atom packings. The structural relationships between these two new clusters and the above Rhl3 species are also discussed.

Analogue of Metallic Lattices in Rhodium Carbonyl Cluster Chemistry. Synthesis and X-ray Structure of the [Rhl2(µ-CO)12]3− and [Rhl4(µ-CO)16(CO)36]4− Anions Showing a Cubic Interconversion

Sir:

We have already reported the isolation and characterization of two members of a family of rhodium carbonyl cluster anions, [Rhl2(CO)12][H5glycine]((2, n = 2, 3), containing a metal atom polyhedron which is part of a hexagonal close-packed lattice.\(^1\) These have been studied by X-ray diffraction\(^4\) and by NMR spectroscopy.\(^3\) We report here the characterization of two new high nuclearity rhodium clusters which show different types of metal atom packings. The structural relationships between these two new clusters and the above Rhl3 species are also discussed.

The mild pyrolysis of Na2[Rhl2(CO)30] or of mixtures of Rh4(CO)12 and NaOH (2.5-3 OH− for every 15 Rh atoms) in 2-propanol under nitrogen at 80 °C for 10-20 h gives a mixture of brown anionic species. Separation is achieved by fractional precipitation of the alkali metal salts from aqueous solution: after precipitation of sodium salts, potassium salts can be obtained from which K3(diglyme)3[Rhl2(CO)12]7− can be separated (15-20% yield) because of its insolubility in diglyme. Metathesis with Me4N+ or Et4N+ chlorides in methanol gives the corresponding crystalline salts; the 1H NMR spectrum of the Et4N+ salt shows the absence of metal hydrides.

The Me4N+ salt has been investigated by X-ray diffraction and the metallic skeleton of the [Rhl2(CO)12]7− anion is illustrated schematically in Figure 1a, while Figure 1b shows the metallic coordination around the central metal atom. The metal atom cluster may formally be derived from the polyhedron of D3h symmetry, which contains that part of the hexagonal close-packed array found in the [Rhl2(CO)12][H5glycine]((2, n = 2, 3) cluster (Figure 2), by capping two square faces ((2, 3, 6, 7) and (9, 11, 13, 14) in Figure 1a). However, while the bottom part of the polyhedron follows this hexagonal close...
The metal atom cluster in the \([\text{Rh}_{15}(\text{CO})_{27}]^{3-}\) anion with the surface metal-metal bonds (a) and the center to surface ones (b). Mean standard deviation 0.005 Å.

Figure 2. A view of the \([\text{Rh}_{15}(\text{CO})_{27}]^{3-}\) anions.

Figure 3. A view of the anion \([\text{Rh}_{15}(\text{CO})_{27}]^{3-}\) showing the carbonyls' stereochemistry.

The metal-metal distances found for \([\text{Rh}_{15}(\text{CO})_{27}]^{3-}\) are rather scattered: there are 36 normal contacts ranging from 2.60 to 2.86 Å (average 2.74 Å), 7 intermediate contacts from 2.90 to 3.00 Å (average 2.94 Å), and 5 long interactions from 3.15 to 3.91 Å.

The complete anion is illustrated in Figure 3. There are 13 terminal and 14 edge-bridging CO groups; all of the skeletal metal atoms except 15, are bonded to three carbonyls. The 13 terminal groups are irregularly distributed; 2 are on metal atom 15 whereas none are on atoms 2 and 3, and the remaining rhodium atoms each contain one terminal carbonyl. The mean values for the Rh–C and C–O bond lengths for terminal and bridging CO are 1.83, 1.17 Å and 2.00, 1.19 Å, respectively.

In acetonitrile, fragmentation of \([\text{Rh}_{15}(\text{CO})_{27}]^{3-}\) occurs on reaction with bromide to give the \([\text{Rh}(\text{CO})_2\text{Br}]^{-}\) and \([\text{Rh}_{14}(\text{CO})_{11}]^{14-}\) anions.

In acetonitrile, fragmentation of \([\text{Rh}_{15}(\text{CO})_{27}]^{3-}\) occurs on reaction with bromide to give the \([\text{Rh}(\text{CO})_2\text{Br}]^{-}\) and \([\text{Rh}_{14}(\text{CO})_{11}]^{14-}\) anions.
metallic crystallites covered (or poisoned) by ligands. Further work is in progress on these families of clusters.

Acknowledgment. We thank the Italian C.N.R. for financial support.

References and Notes


4. The salt [Me₄N]₃[Rh₁₅(CO)₂₇] crystallizes in the monoclinic space group P2₁/n (No. 14) with cell constants a = 21.058 (4) Å, b = 22.485 (9) Å, c = 22.848 (6) Å, β = 91.52 (3)°, Z = 4. The structure has been solved by direct methods and refined by least squares using 3730 independent significant counter data. The refinements are in progress, the current R value being 8.3%.

5. The salt [Et₄N]₄[Rh₁₅(CO)₂₇] crystallizes in the tetragonal space group P4/ncn (No. 135) with cell constants a = 27.186 (4) Å, c = 8.3% of the independent significant counter data. The refinements are in progress, the current R value being 5.2%.


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Diel-Alder Cycloaddition of Juglone Derivatives: Elucidation of Factors Influencing Regiochemical Control

Sir:

In connection with studies directed toward tetracycline total synthesis, Inhoffen and Muxfeldt reported an interesting observation: the nature of the oxygen function in 5-hydroxy-1,4-naphthoquinone profoundly influenced the regiochemistry of the cycloaddition with 1-acetoxybutadiene. This general trend has been noted subsequently for a variety of diene systems by several groups, notably Birch, Kelly, and Tröst.

The rationale for this effect, alluded to initially by Inhoffen and further developed by Birch and Kelly, revolves around the concept that the strong hydrogen bond known to be present in quinone 1 serves as an “internal Lewis acid” polarizing the unsaturated system and resulting in the C-4 carbonyl serving as the dominant director of cycloaddition. Alternatively, electron donation by the oxygen is considered to dominate in the regiochemistry of the cycloaddition with 1-acetoxybutadiene. This general trend has been noted subsequently for a variety of diene systems by several groups, notably Birch, Kelly, and Tröst.

The rationale for this effect, alluded to initially by Inhoffen and further developed by Birch and Kelly, revolves around the concept that the strong hydrogen bond known to be present in quinone 1 serves as an “internal Lewis acid” polarizing the unsaturated system and resulting in the C-4 carbonyl serving as the dominant director of cycloaddition. Alternatively, electron donation by the oxygen is considered to dominate in the acetate 2 (and methyl ether 6) leading to reversal of the regiochemical result.