distortion of the porphyrin from planarity. The other anti-$Fe^{3+}$ porphyrin antibody, 13C4, demonstrates a four order of magnitude range of affinities for TCPP containing different metals, but the unmetalated porphyrin is one of those more tightly bound. Moreover, the $Zn^{2+}$ and $Sn^{4+}$ porphyrins, bound most weakly to 13C4, are among the most tightly bound to 13B4. A four order of magnitude range of affinities has also been observed in the binding of monoclonal antibodies to EDTA complexes of various metals.[17] The same range of affinities in anti-porphyrin antibodies is perhaps more surprising because the EDTA ligand is much more capable of conformational variability.

In summary, we have shown that monoclonal antibodies that bind tightly to porphyrins can be elicited. There is a large range of affinities possible for various metals, evidence of some kind of interaction, between metal and protein in antibody–porphyrin complexes, which may perturb the reactivity of a metalloporphyrin. Of particular importance for predictive correlations is the observation that in each case the metalloporphyrin used as the antigen is bound more tightly than the other porphyrins tested. We have shown that these antibodies can bind tightly to other metalloporphyrins related to the antigen. This is important because a catalytic porphyrin–antibody complex could result from immunization with a porphyrin containing a noncatalytic metal, chosen to stably bind a substrate. The next important step will be to bind a substrate as well as a porphyrin in an antibody binding pocket. Given more than 600 Å$^2$ of surface contact seen in antibody–protein complexes,[18] this may be possible.

**Acknowledgment.** This work was supported in part by the American Cancer Society in the form of a Postdoctoral Fellowship to A.W.S. We thank Diane Schloeder for advice on tissue culture.

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# Alkyne Hydrogenation by a Dihydrogen Complex: Synthesis and Structure of an Unusual Iridium/Butyne Complex

Gregory Marinelli,† Idris El-Idrissi Rachidi,‡
William E. Streib,† Odile Eisenstein,*,‡ and
Kenneth G. Caulton*,†

*Department of Chemistry and Molecular Structure Center*
*Indiana University, Bloomington, Indiana 47405*
*Laboratoire de Chimie Théorique, Bâtiment 490*
*Centre de Paris-Sud, 91405 Orsay, France*

*Received November 7, 1988*

The $\eta^2$-$H_2$ ligand in $IrH_4P_3^+$ (P = $PMe_2Ph$) serves, in an equilibrium process, as a "good leaving group" and provides the rare *unsaturated* hydride complex $IrH_2P_3^+$. We reported earlier[1] the utilization of this species in a cycle for hydrogenation of ethylene at 25 °C and 1 atm. We describe here the use of this reagent for selective hydrogenation of 2-butyne, which leads to isolation of a butyne complex of remarkable structure.

Treatment of $[IrH_4P_3]BF_4$ in $CH_2Cl_2$ with 5 equiv of 2-butyne yields, as the only metal-containing product, $Ir(MeC_2Me)P_3BF_4$,[2] together with a mixture of *cis*-2-butene and 1-butene. Neither *trans*-2-butene nor butane is detected ($^1H$ NMR). The $^1H$ NMR of this complex in $CD_2Cl_2$ shows only a single P-*Me* doublet at 22 °C, and the $^{31}P\{^1H\}$ NMR is a singlet from 22 °C to −95 °C. The apparent equivalence of the three phosphines,[3] which is reinforced by the quartet structure of both the Ir–C $^{13}C$ and the butyne proton signals, is surprising since we anticipated a structure based upon planar Ir(I) and a T-shaped $IrP_3$ fragment. We therefore determined the solid-state structure of $Ir(MeC_2Me)(PMe_2Ph)_3BF_4$ by X-ray diffraction,[4] which reveals noninteracting cations and $BF_4$ anions. The cation (Figure 1) has a structure which is neither planar nor tetrahedral: the $IrP_3$ fragment is distinctly nonplanar but also deviates markedly from $C_3$ symmetry.[5] The IrP(20) distance is 0.07 Å shorter than the two statistically equivalent IrP(2) and IrP(11) distances. Consistent with this approximate mirror symmetry are the PIrP angles, with those involving P(20) smaller (at 90.6 (1) and 94.0 (1)°) than those between P(2) and P(11) (106.1 (1)°). The line of the alkyne multiple bond is approximately parallel to the P(2)/P(11) vector. Thus, one description of the coordination geometry is square pyramidal (counting each alkyne carbon as one basal site of the polyhedron and P(20) as apical). The Ir–C distances are both very short (average value 2.015 (6) Å),[6] consistent with multiple bonds. The $^{13}C$ chemical shift of the alkyne carbons, 170.6 ppm, is in the range of four-electron donor alkynes.[7]

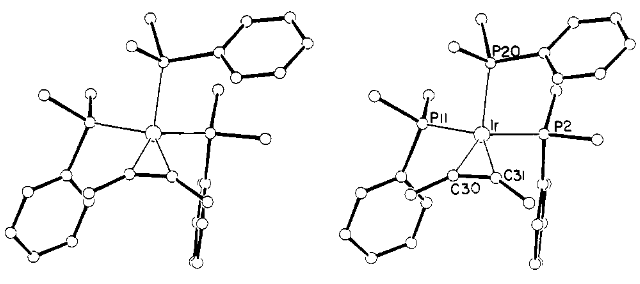
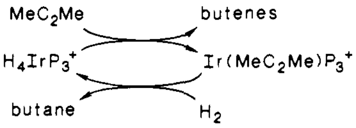


Figure 1. Stereo ORTEP drawing of $Ir(MeC_2Me)(PMe_2Ph)_3^+$, omitting hydrogen atoms. Selected structural parameters: Ir–P2, 2.309 (2); Ir–P11, 2.312 (2); Ir–P20, 2.236 (2); Ir–C30, 2.016 (5); Ir–C31, 2.014 (6); C30–C31, 1.306 (8) Å.

**Scheme I**



Bonding in the experimental (idealized $C_s$) structure was compared to idealized $T_d$ and square-planar structures using extended Hückel theory calculations. This reveals the acetylene to be most tightly bound to the metal fragment (i.e., greater forward and back electron transfer) in the $C_s$ structure. The differences originate in the superior match of the orbitals of the bent acetylene with $IrP_3^+$ in the $C_s$ structure. The relevant donor orbitals of cis-bent acetylene ($\pi_\parallel$, in the $IrC_2$ plane and $\pi_\perp$, orthogonal to $\pi_\parallel$) are close in energy.[8] Of the two possible acetylene acceptor orbitals, only $\pi_\parallel{}^*$ is really effective. The "best prepared" $d^8ML_3$ fragment should therefore have two low-lying empty orbitals complementary to the symmetry of $\pi_\parallel$ and $\pi_\perp$ and a high-lying occupied orbital adapted to $\pi_\parallel{}^*$. The T-shaped $IrP_3^+$ fragment (leading to a square-planar structure) lacks the empty

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† Indiana University.

‡ Centre de Paris-Sud.

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(2) NMR data (omitting phenyl resonances): $^1H$ NMR (360 MHz, 22 °C, $CD_2Cl_2$) $\delta = 2.85$ (q, $^4J_{P\text{-}Me} = 3$ Hz, 3 H); 1.66 (d, $^2J_{P\text{-}Me} = 10$ Hz, 18 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CD_2Cl_2$) $\delta = 170.6$ (q, $^2J_{PC} = 5$ Hz, *C*-Me), 19.9 (d, $^1J_{PMe} = 35$ Hz), 18.5 (s, C-*C*$H_3$); $^{31}P$ NMR (146 MHz, 22 °C, $CH_2Cl_2$) $\delta = -16.8$ (s). Yield of isolated product: 45%. Satisfactory elemental analysis was obtained for C, H, and P.

(3) A similarly simple spectrum is found in benzene-$d_6$ although the butyne methyl protons are shifted 0.4 ppm upfield from the value in $CD_2Cl_2$. The fact that this $BF_4^-$ compound is soluble in benzene is, of course, surprising, and perhaps indicative of a structure with coordinated $BF_4^-$.

(4) Crystal data for $[Ir(MeC_2Me)(PMe_2Ph)_3]BF_4$ (−139 °C): $a = 11.601$ (1) Å; $b = 13.855$ (1) Å; $c = 19.138$ (3) Å; $\beta = 99.66$ (1)°; $Z = 4$ in space group $P2_1/n$. $R(F) = 0.0268$ for 3610 reflections with $F > 3\sigma(F)$.

(5) A relevant comparison compound is $Co(PhC_2Ph)(PMe_3)_3^+$. See: Capelle, B.; Dartiguenave, M.; Dartiguenave, Y.; Beauchamp, A. *J. Am. Chem. Soc.* **1983**, *105*, 4662.

(6) Compare the Ir–C distance (2.159 Å) in *fac*-$IrMe_3(PMe_2Ph)_3$.

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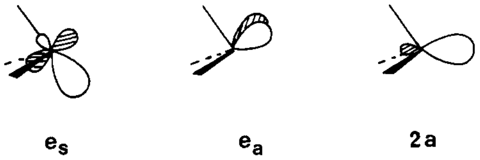
orbital to match $\pi_\perp$ and thus constrains the acetylene to two-electron donation. The pyramidal $IrP_3^+$ fragment (leading to $T_d$ or $C_s$) has the requisite three orbitals in the form of the 2e and 2a of a regular $C_{3v}$ $IrP_3^+$ pyramid:[9] $e_s$ (one of the 2e set) matches $\pi_\perp$, 2a matches $\pi_\parallel$, and $e_a$ (from the 2e pair) is close in energy to $\pi_\parallel^*$. The acetylene is thus a formal four-electron donor. Optimizing this last interaction significantly increases the metal/acetylene bonding, and this is accomplished by pointing the two lobes of the $e_a$ more toward the acetylene carbons. In terms of nuclear motions, this is achieved by bending the two Ir–P bonds toward the $IrC_2$ plane, which converts the $T_d$ to the $C_s$ structure.



Reaction of $Ir(MeC_2Me)P_3^+$ with $H_2$ (1 atm) at 25 °C in $CD_2Cl_2$ yields butane (no butenes) and $IrH_4P_3^+$, which closes the cycle of Scheme I. Further mechanistic details of the steps in this scheme, together with a broader survey of the reactivity of $Ir(MeC_2Me)P_3^+$, are currently under investigation.

**Acknowledgment.** We thank the NSF (Grant No. 8707055) for financial support and Johnson-Matthey Co. for material support. O.E. acknowledges the Indiana University Institute for Advanced Study for a fellowship which enabled this collaboration. Scott Horn is thanked for skilled technical assistance. The Laboratoire de Chimie Thêorique is associated with the CNRS (UA506) and is a member of ICMO and IPCM.

**Supplementary Material Available:** Tables of positional and thermal parameters for $[Ir(MeC_2Me)(PMe_2Ph)_3]BF_4$ and a figure showing thermal ellipsoids (5 pages). Ordering information is given on any current masthead page.

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## Life Span of a Local Structure in Colloidal Suspensions

Kensaku Ito, Hiroya Okumura, Hiroshi Yoshida, and
Norio Ise*

*Department of Polymer Chemistry*
*Kyoto University, Kyoto 606, Japan*
*Received September 19, 1988*

The existence of local ordered structures in colloidal suspensions has been confirmed by various techniques,[1-7] but only the static aspect of the structure has been described except in a few papers, as was reviewed recently.[8] In the present paper, we describe the life span of the local ordered structure which has not been discussed before but is of great significance to the complete understanding of the colloidal phenomena.

Polystyrene latex, purchased from the Sekisui Chemical Company (N300, diameter: $0.32 \times 10^{-6}$ m, charge density: $1.8 \times 10^{-6}$ C/cm$^2$), was thoroughly purified as described earlier[8,9] before use. The micrographs showing particle distributions were taken at a fixed position of the suspensions (0.5%) at room temperature by the ultramicroscope (AXIOMAT IAC, Carl Zeiss, Oberkochen, FRG) and digitized by the image processing system (IBAS) of the same company. The particle positions were determined at an interval of 1/30 s (at every video frame) and fed into a personal computer (PC9801, NEC). The interparticle distance ($2D_{exp}$) was estimated to be $1.16 \times 10^{-6}$ m by Fourier patterns of the particle distribution.[10] The $2D_{exp}$ was smaller than the average interparticle spacing ($2D_0$, $1.69 \times 10^{-6}$ m) and practically constant with time through the growing process. A regular triangle with a side of $2D_{exp}$ was defined as an elementary unit of the ordered structure, because the (111) plane of the face-centered cubic lattice was observed in the present experiments. An uncertainty of 15% in the length of the side was taken into consideration, which seems reasonable in light of thermal vibration of the particles and distortion of the lattice in the ordered structure.[8] After NaCl was added to a purified suspension up to $1.0 \times 10^{-4}$ M, the crystallization was allowed to take place by putting ion-exchange resin beads into the suspension. During the first 2 h, the electric conductivity decreased with time and thereafter became nearly constant, which indicates the almost complete removal of added NaCl.

**Table I.** Distribution of Life Span of Core Particles

| time (×1/30 s) | 24 h (%) | 48 h (%) |
|---|---|---|
| 1 | 69.3 | 58.0 |
| 2 | 20.0 | 13.9 |
| 3 | 6.7 | 8.3 |
| 4 | 2.7 | 8.3 |
| 5 | 1.3 | 5.2 |
| 6 | | 2.4 |
| 7 | | 1.0 |
| 8 | | 0.7 |
| 9 | | 0.7 |
| 10 | | 1.4 |

The elementary units appeared even at 1 h after the addition of the ion-exchange beads. The units (triangles) were found on the micrograph sporadically, and the appearance and disappearance of the units were observed at every video frame. The same situation was also observed at 6 h. Clusters of elementary units were observed at 24 h, and a halo pattern was obtained by the 2-D Fourier transformation therefrom. The clusters grew further at 48 h and became large lattices at 72 h. Figure 1 shows the elementary units defined above at 24 and 48 h. The isolated dots in each figure represent the particles which were not involved in the clusters. The average numbers of the elementary units per cluster were about 12 at 24 h and 30 at 48 h. Most clusters assumed different shapes at every video frame. While the clusters are large, their central part was left unchanged whereas surrounding parts disappeared. Rather small clusters became smaller and finally disappeared. The number of bonds of one particle varied accordingly. To measure this number, we adopted tentatively the following procedure. The particles having six bonds were defined as core particles. The number of bonds of each core particle was followed up to 10 consecutive video frames (for 1/3 s). The period in which the core particles maintained six bonds was measured as the life span of the clusters. Table I shows the life span measured at 24 and 48 h. About 69% of the core particles lost at least one bond in 1/30 s at 24 h, and the longest life span was 5/30 s. At 48 h, 58% of the core particles also lost the bonds in 1/30 s. The number of particles with a longer life span (longer than 3/30 s) was larger at 48 h than at 24 h. At 48 h, 1.4% of the core particles lived longer than 1/3 s. That is, at 24 h, the clusters disappeared before 5/30 s, although at 48 h some of the clusters did not disappear but seemed to grow further.

In the present conditions, the so-called Kossel mechanism[11] of crystal growth was not observed. Instead, the life span of the clusters depended mainly on the size of the clusters. This tendency coincides, at least qualitatively, with the mode of crystallization

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