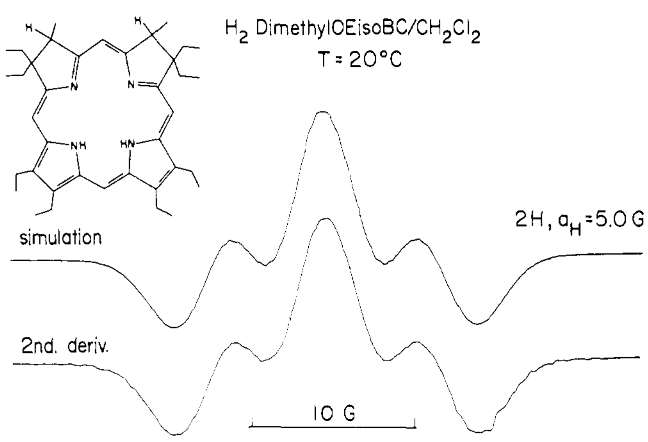

Figure 5. Second derivative ESR spectra, in CH_2Cl_2, of $H_2DMeOEiBC^{+}\cdot ClO_4^-$. The simulation demonstrates that two equivalent protons determine the spectral pattern observed. The peak-to-peak line width of the first derivative signal is ~10 G.

spectrum requires two additional sets of two nitrogens with a_N = 1.8 and 0.9 G. (Nitrogen hyperfine constants reflect[8] the spin density at the adjacent carbons as well as at the nitrogen itself.)

Confirmation of these assignments is obtained by partial exchange of the protons on the reduced rings with deuterons, by treatment of ZnTPiBC with potassium in *tert*-butyl alcohol-d_1 according to Whitlock and Oester.[12] The ESR spectrum of the resulting deuterated species is shown in Figure 4. The spectrum has collapsed significantly compared with that of $ZnTPiBC^{+}\cdot$ (Figure 2) as expected from the difference in gyromagnetic ratios and nuclear spins of hydrogen and deuterium ($I = {}^1/_2$ and 1, $a_D = 0.1535 a_H$). The spectrum of Figure 4 can be fitted by a simulation which maintains the nitrogen and small proton splittings and assumes the indicated distribution of partial deuteration at the reduced rings. These results clearly confirm the assignments of the eight large proton splittings as arising from the reduced rings. Further support of these conclusions derives from the cation of $H_2DMeOEiBC$, which contains only two protons on the reduced rings and whose three-line ESR spectrum (Figure 5) of intensities 1:2:1 is unambiguously attributable to two equivalent protons of a_H = 5 G. Although the multitude of smaller splittings expected from the nitrogens, meso protons, and methylene amd methyl groups is not resolved, spin densities at these positions, comparable with those found in $ZnTPiBC^{+}\cdot$, can readily be accommodated within the envelope of the $H_2DMeOEiBC^{+}\cdot$ spectrum.

Half-wave potentials for isobacteriochlorins, measured by cyclic voltammetry, are listed in Table I and contrasted there with those of analogous chlorins and porphyrins. The notable features of these results are the significant cathodic shifts of the redox potentials: the isobacteriochlorins are considerably easier to oxidize and harder to reduce than the corresponding chlorins and porphyrins. (Note that the redox span between the first ring oxidation and reduction potentials ($\Delta E_{\pm}$) remains insensitive to hydrogenation of the pyrrole rings.)

Table I. Redox Potentials of Isobacteriochlorins[a] ($E_{1/2}$ vs. SCE)

compound	oxidation 2	oxidation 1	reduction 1	reduction 2	$\lvert\Delta E_{\pm}\rvert$[b]
H_2TPiBC	0.95	0.57	−1.52		2.09
ZnTPiBC	0.69	0.28	−1.73		2.01
CuTPiBC	0.75	0.40			
$H_2DMeOEiBC$	0.96	0.37	−1.72		2.09
ZnDMeOEiBC	0.66	0.08	−1.95		2.03
H_2TPP[c]	1.28	0.95	−1.05	−1.47	2.00
ZnTPP[c]	1.03	0.71	−1.35	−1.80	2.06
CuTPP[c]	1.16	0.90	−1.20	−1.68	2.10
H_2OEP[c]	1.32	0.83	−1.45	−1.87	2.28
H_2 etiochlorin 1	1.16	0.65	−1.42	−1.86	2.07
Zn etiochlorin 1	0.84	0.35	−1.60		1.95

[a] Oxidations in CH_2Cl_2 or butyronitrile, reductions in butyronitrile (0.1 M tetra-*n*-butylammonium perchlorate). [b] E_1(oxidn) − E_1(redn). [c] Literature values from ref 13.

These properties may dictate the choice of the isobacteriochlorin framework for the multielectron transfers in nitrite and sulfite reductases and suggest that siroheme may function via π cation radicals. Such radicals should display the optical and ESR properties described here (Figures 1 and 5). Furthermore, the peripheral unpaired spin density distribution calculated and found in the model compounds indicates that NMR spectra of these radicals should exhibit significant contact shifts and line broadening.

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Iridium Complexes in Alkane Dehydrogenation

Sir:

The functionalization of alkanes under mild conditions by soluble transition-metal compounds is a challenging problem.[1]

In this connection, we have been studying, in noncoordi-

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nating solvents, systems in which the metal is stabilized by the minimum number (usually two) of permanently bound tertiary phosphine ligands.[2,3] We hope in this way to mimic, in solution, the ligand-deficient coordination environment of an exposed metal atom at a discontinuity in the surface of a heterogeneous catalyst. The latter are well known to be particularly active catalysts for many reactions which include alkane activation steps.[1]

We now report some observations on a number of iridium complexes, and on some related alkene and alkane dehydrogenation reactions. The complexes involved, $[IrH_2(olefin)_2L_2]^+$ (**1**, L = PPh_3), are of interest not only because they are the first examples of monoolefin-dihydrido complexes, but also because they appear to be the active intermediates in the hydrogenation system which we have previously described.[2-4]

In a noncoordinating solvent, such as CD_2Cl_2, monoolefins such as cyclooctene (coe, 10 mol equiv) are able to displace the coordinated solvent from $[IrH_2(acetone)_2L_2]BF_4]$ (**2**, L = PPh_3)[2] at −60 °C to give $[IrH_2(coe)_2L_2]^+$ quantitatively, in a smooth, clean process. These reactions can be conveniently followed in an NMR experiment using a Brucker 270-MHz instrument.

The first-formed isomer is *cis,cis,trans*-$[IrH_2(coe)_2L_2]^+$ (**1a**). This we identified from its ^{1}H NMR spectrum at −60 °C and by comparison with the properties of the related diolefin analogues, $[IrH_2(cod)L_2]^+$ (**3**, cod = 1,5-cyclooctadiene), which we have previously described.[5] At −35 °C, **1a** isomerizes to an equilibrium mixture of **1a** and **1b** (~60:40). **1b** is the trans isomer.[5] ^{1}H NMR data (reported as position (δ, parts per million) (multiplicity, coupling constant in hertz, assignment)): **1a**, −12.2 (triplet, 19, IrH), 4.0 (complex, coe vinyl); **1b**, −10.25 (triplet, 24, IrH), 3.7 (complex, coe vinyl).

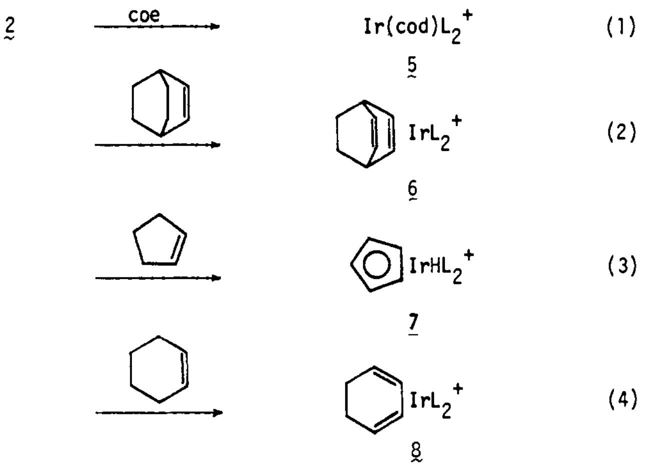
On heating to −10 °C, the colorless solution of **1a** and **1b** becomes red. If the reaction is performed in the presence of excess olefin, a single product, *trans*-$[Ir(coe)_2L_2]^+$ (**4**), is formed:[6] ^{1}H NMR 4.2 (complex, coe vinyl); ^{1}H decoupled ^{13}C NMR 86 (singlet, coe vinyl). The complex adds H_2 at −80 °C quantitatively giving the cis,cis,trans adduct **1a**.

Other olefins, such as styrene and ethylene, behave similarly. Above −35 °C, styrene gives both isomers (**1a** and **b**), while ethylene gives only the cis,cis,trans isomer **1a**. Presumably, steric repulsion between the olefin ligands dictates the relative stabilities of **1a** and **1b**.

Interestingly, the ethylene complex only transfers hydrogen to the coordinated olefin at a temperature (+10 °C) 20 °C higher than do the others. Possibly, the metal-olefin bond is stronger for ethylene than for the others, and the approach to the transition state for insertion correspondingly more difficult.

Over several hours, new peaks begin to appear in the ^{1}H NMR spectrum of the cyclooctene complex **4**. These peaks correspond to the cycloocta*diene* complex $[Ir(cod)L_2]^+$ (**5**) and to free cyclooctane. This observation made us suspect that complexes of type **4** might be active for hydrocarbon dehydrogenation under mild conditions. After reflux in CH_2Cl_2 (40 °C) for 30 min, **4** is quantitatively converted into **5**,[7] and the recrystallized complex (75% yield) proved to be identical in all respects with an authentic sample of **5**.

Other alkenes also react in this way to give novel diene complexes. [2.2.2]Bicyclooctene smoothly reacts with **2** in refluxing CH_2Cl_2 for 6 h to give essentially quantitative yields of the new bicyclooctadiene complex **6**:[7] ^{1}H NMR 4.55 (broad, allyl CH), 3.65 (broad, vinyl CH), 0.95 (broad, CH_2). The metal cannot give a π-allyl intermediate in this case, owing to the cage structure of the alkene, so that the metal must be directly activating the CH bonds of the paraffinic chain of the substrate.



Cyclopentene gives the new cyclopentadienyl complex **7**[7] under similar conditions after 40 min. The ^{1}H NMR spectrum of the complex (−14.4 (triplet, 36, IrH), 5.15 (singlet, Cp)) is similar to those of the known cobalt and rhodium analogues.[8]

Cyclohexene gives the new cyclohexadiene complex **8**: ^{1}H NMR 5.3 and 5.9 (broad, CH), 1.6 (broad CH_2).[7] No benzene complex could be detected.

In each case, the organic products of the reactions are the corresponding alkanes (GC, ^{1}H NMR). Complexes **5–8** were recrystallized in 60–75% yield and were also independently synthesised (diene + **2**, 40 °C).

Reactions of this type may be general,[9] in which case they may constitute a useful synthetic route to unusual alkene and alkenyl complexes. Related catalytic reactions are also known.[10]

We have also found that the activation even of alkanes is possible with this system. Cyclopentane, for example, gives the cyclopentadienyl complex **7**[7] (30% yield by ^{1}H NMR, 5% isolated yield) after 18 h, in refluxing 1,2-dichloroethane containing 3,3-dimethyl-1-butene (**9**) as hydrogen acceptor. The reaction is essentially a hydrogen transfer from the cycloalkane to the alkene. In a typical run, $[IrH_2(acetone)_2(PPh_3)_2]BF_4$ (200 mg) was treated with 3,3-dimethyl-1-butene (8 mol/Ir) and cyclopentane (2 mL) in 1,2-dichloroethane (20 mL). The solution turned red after 20 min. After 18 h at reflux under N_2, ^{1}H NMR analysis of the involatile residues showed the presence of **7** (30% yield). **7** was crystallized in 5% yield and identified by a comparison with an authentic sample (^{1}H NMR, IR, analysis). The reaction mixture appeared completely homogeneous throughout the reaction.

Cyclooctane, under similar conditions,[11] gives the cyclooctadiene complex **5** after 4 h: 70% yield by ^{1}H NMR, 50% isolated yield; ^{1}H NMR 4.14 (broad, cod vinyl), 2.36 and 2.01 (complex, cod allyl). **5** has been isolated in good yield from these reaction mixtures in a completely pure state, and its identity has been confirmed by its reaction with HCl, in $CDCl_3$ at 20 °C when the characteristic[12] hydride and (cod) vinyl ^{1}H NMR resonances of $[IrHCl_2(cod)L]$ were observed.

3,3-Dimethyl-1-butene (**9**) seems to be indispensable as hydrogen acceptor for this reaction. An olefin having allylic hydrogens and capable of being dehydrogenated, as in eq 1-4, completely inhibits paraffin dehydrogenation. Olefins smaller than **9**, such as ethylene, styrene, or trimethylvinylsilane, instantly turn the reaction mixture red with the formation of the stable $[Ir(olefin)_2L_2]^+$ cations of type **4**. These complexes do not react with alkanes, presumably because the olefins are too tightly bound to allow access of the alkane to the metal. Larger olefins, much as tetraphenylethylene, do not appear to react at all with the solvate hydride **2**.

Only in the case of **9** do we find alkane dehydrogenation reactions. The reaction mixture turns red only after 20 min at reflux. We imagine that the resulting olefin complex of **9** is unstable and readily dissociates olefin to allow the alkane access to the active site.[12]

Alternative interpretations of our results can be envisaged.[13] Trace acid, for example, might protonate **9** and the resulting carbonium ion dehydrogenate the cycloalkanes. We find, however, that the deliberate addition of trace acid to the system completely inhibits the activation, and that some **7** (~7%) is formed from cyclopentane in the absence of **9**.

Even though the reaction mixtures appear entirely homogeneous, colloidal iridium might still have been formed and be the true active species.[13] Metallic Ir, like Pt and Rh, can indeed be active for H/D exchange in alkanes[14] under mild conditions, and for cycloalkane dehydrogenation[15] above ~150 °C. We have not yet been able to eliminate this possibility definitively. If true, however, this hypothesis is difficult to reconcile with our observation of activity only with **9** as hydrogen acceptor (or, in the case of cyclopentane, without a hydrogen acceptor), rather than with other olefins. We have also done photon-correlation light-scattering experiments to explore this question: our measurements showed no evidence for the presence of any colloid in the reaction mixtures.

That our system is so active in alkane dehydrogenation may be related to its unprecedented activity[2,3] for the reverse reaction, alkene hydrogenation.

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Laser Photolysis Study of the Exciplex between Triplet Benzil and Triethylamine

Sir:

The behavior and properties of exciplexes is a subject of current interest; they are frequently proposed as reaction intermediates in singlet- and triplet-state processes.[1,2] The former have been characterized in more detail, largely because many singlet exciplexes are strongly fluorescent,[3] although some absorption studies using laser flash photolysis have also been carried out.[2] Triplet-derived exciplexes do not usually luminesce, and as a result their direct characterization is more difficult; they have been observed directly in very few systems,[4] e.g., zinc ethioporphyrin I-hexachloroethane, where the exciplex absorption spectrum resembles that of the porphyrin triplet.[4]

One of the photochemical systems where the intermediacy of triplet-derived exciplexes is most strongly supported by indirect evidence is the quenching and/or photoreduction of triplet carbonyls by amines;[5,6] no direct evidence for the intermediacy of exciplexes has been reported in these systems.[7]

Triplet benzil has a T-T absorption spectrum quite different from that of benzil radical anion,[8] therefore allowing the independent study of triplet decay and radical-ion formation in benzil-amine systems using nanosecond laser flash photolysis techniques. Using this approach, we have examined the triethylamine (TEA)-benzil system in wet acetonitrile and observed that, under conditions of short triplet lifetime (i.e., high TEA concentration), the formation of benzil radical anion is considerably slower than the decay of the triplet state; we attribute this "delay" to the intermediacy of a relatively stable exciplex, whose properties are reported in this study.

The effect mentioned above is observed over a wide range of water-acetonitrile compositions, with the exciplex lifetime being apparently longer the higher the water content. At the same time the increase in water content seems to favor the formation of ground-state complexes (from UV spectroscopy studies). The results reported herein have been obtained in 12:88 water-acetonitrile (v/v) mixture containing 0.003 M sodium hydroxide.[9] In this mixture we do not observe any ground-state complexation;[10] at the same time, the presence of a strong base assures that the basicity of the medium will not be changed by the addition of amine. The rate of triplet quenching was monitored at 450 nm, examining the decay of the signal (due to T-T absorption) as a function of TEA concentration, and led to $k_q = 1.3 \times 10^9\ M^{-1}\,s^{-1}$.[11] That is, in the presence of 0.1 M TEA, the triplet lifetime will be $\tau_T < 8$ ns; when under these conditions we monitor transient absorptions

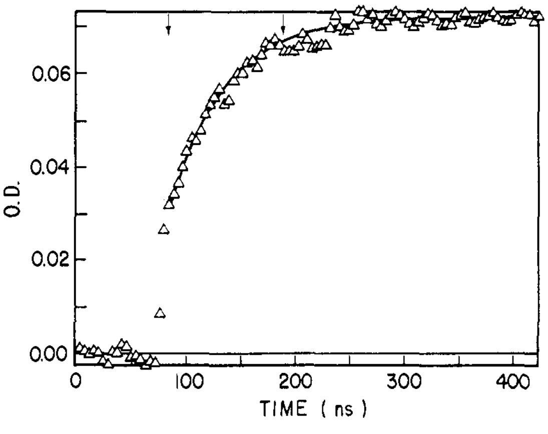

Figure 1. Time profile showing the increase in optical density at 570 nm following laser excitation of benzil in the presence of 0.1 M TEA. The arrows indicate the section of the curve used to determine the exciplex lifetime.

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