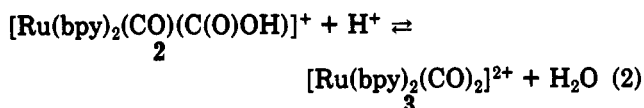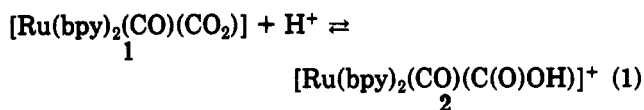complexes have been proposed as active species in electrochemical and photochemical CO_2 reductions.[2a] We have reported the molecular structure of an η^1-CO_2 complex of ruthenium, [Ru(bpy)$_2$(CO)(CO$_2$)]·3H$_2$O[8] (bpy = 2,2'-bipyridine) (1), which exists as equilibrium mixtures with [Ru(bpy)$_2$(CO)(C(O)OH)]$^+$ (2) and [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ (3) in H$_2$O[9] (eqs 1 and 2). 2 and 3 are possible precursors for

$$[Ru(bpy)_2(CO)(CO_2)] + H^+ \rightleftharpoons$$
$$\mathbf{1}$$
$$[Ru(bpy)_2(CO)(C(O)OH)]^+ \quad (1)$$
$$\mathbf{2}$$

$$[Ru(bpy)_2(CO)(C(O)OH)]^+ + H^+ \rightleftharpoons$$
$$\mathbf{2}$$
$$[Ru(bpy)_2(CO)_2]^{2+} + H_2O \quad (2)$$
$$\mathbf{3}$$

the formation of CO and HCOO$^-$, respectively, in electrochemical[10] and photochemical[11] CO_2 reduction. Disproportionation of 2 to 1 and 3 in an aqueous and an organic solution caused serious difficulties in growing single crystals of 2. The molecular structure of [Ru(bpy)$_2$-(CO)(C(O)OCH$_3$)]$^+$ as a model compound for 2, therefore, is of great interest from the viewpoint of elucidation of the interconversion between 1 and 2 by a diffusion-controlled reaction. This communication reports the crystal structure of [Ru(bpy)$_2$(CO)(C(O)OCH$_3$)](B(C$_6$H$_5$)$_4$)·CH$_3$CN (4) and comparison of the bond characters between Ru–C(O)OCH$_3$ in 4 and Ru–CO$_2$ in 1.

The reaction of 1 with CH$_3$I in CH$_3$OH affords [Ru-(bpy)$_2$(CO)(C(O)OCH$_3$)]I in almost quantitative yield, and the PF$_6$ salt of 4 is also synthesized by the reaction of the PF$_6$ salt of 3 with CH$_3$ONa.[9] Single crystals of 4 were obtained by slow evaporation of an acetonitrile solution containing the (B(C$_6$H$_5$)$_4$)$_2$ salt of 3 and 1 equiv of CH$_3$O-Na. The Ru atom is octahedrally coordinated, and the methoxycarbonyl moiety is in a cis position with the carbonyl ligand (Figure 1).[12] The bond distances and angles

for the 2,2'-bipyridine ligands of 4 are similar to those for 1 and also close to those of the other 2,2'-bipyridine complexes of ruthenium.[13] The C1–O1 and C1–O2 bond distances for 4 are 1.191 (8) and 1.344 (8) Å, respectively. It is worthy of note that the average of the C1–O1 and C1–O2 bonds (1.268 Å) for 4 is essentially same as that of the two C–O bonds in the CO_2 moiety of 1 (1.264 Å). The Ru–C1 distance (2.042 (6) Å) for 4 is close to the metal–carbon bond distance for the previously reported (methoxycarbonyl)rhodium complex (2.041 (5) Å).[14] The fact, however, that the Ru–C1 distance for 4 is shorter than the Ru–CO$_2$ bond distance for 1 (2.064 (13) Å) indicates that the multibond character of the Ru–C(O)OCH$_3$ bond in 4 is not smaller than that of the Ru–CO$_2$ bond of 1, although a metal–CO$_2$ bond in [W(CO)$_5$(η^1-CO$_2$)]$^{2-}$ is proposed to have a carbene character (W=CO$_2^{2-}$) of the Fisher type.[15] On the basis of the similarity of the ^{13}C NMR chemical shifts of the carbonyl and methoxycarbonyl carbons (δ 202.2 and 206.8) of 4[16] with those of the carbonyl and hydroxycarbonyl carbons of 2 (δ 201.5 and 205.1) in CD$_3$OD, the electronic structure of the methoxycarbonyl carbon of 4 may be close to that of the hydroxycarbonyl carbon of 2. This assumption implies that a negative charge resulting from dissociation of the proton from the hydroxycarbonyl moiety of 2 (eq 1) is mainly localized on the CO_2 group of 1 rather than delocalized on the RuCO$_2$ moiety. The localization may enable a smooth reversible conversion to 2 in H$_2$O (eq 1), similar to the case for organic carboxylic acids.

Supplementary Material Available: For this structure study, tables of atomic parameters and U values (4 pages). Ordering information is given on any current masthead page.

OM9203789

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(12) Crystal data for 4: C$_{49}$H$_{42}$O$_3$N$_5$BRu, M_r = 860.77, triclinic space group P1, a = 9.548 (3) Å, b = 13.004 (5) Å, c = 17.743 (4) Å, α = 77.26 (3)°, β = 74.89 (2)°, γ = 83.64 (3)°, V = 2071.1 (12) Å^3, Z = 2, D_c = 1.380 g cm^{-3}, $F(000)$ = 844, λ = 0.709 30 Å, μ(Mo Kα) = 4.25 cm^{-1}, crystal dimensions 0.03 × 0.25 × 0.30 mm. R_F = 0.045 for 7219 unique reflections with $F > 2\sigma(F)$ and 532 variables. Data were collected by θ–2θ techniques (0 < 2θ < 50°) on an Enraf-Nonius CAD4-GX21 automated four-circle diffractometer with Mo Kα radiation. The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as fixed contributions.

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Phase-Transfer Photolysis of Metal Hexacarbonyls

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Summary: The photochemical conversion of M(CO)$_6$ (M = Cr, Mo, W) to M(CO)$_5$X$^-$ (X = halogen) across a hexane/water interface leads to a separation of the reactant and product. This process may be of general importance for synthetic applications. Under suitable conditions inner-filter effects and secondary photolysis can be avoided.

Photochemical reactions in microheterogeneous media have been investigated extensively.[1,2] In particular excited-state electron transfer of metal complexes has been

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Table I. Data for Photochemical Conversion of M(CO)₆ to M(CO)₅X⁻ (X = Cl, Br, I) by Phase-Transfer Photolysis from n-Hexane to Water

reactants[a]	λ_{irr} (nm)	product[b]	λ_{max} (ϵ)[c]
Cr(CO)₆ + NaBr	290–370	Cr(CO)₅Br⁻	443 (840), 248 (24 000)
Cr(CO)₆ + NaI	366	Cr(CO)₅I⁻	438 (1000), 348 (200)
Mo(CO)₆ + NaCl	290–370	Mo(CO)₅Cl⁻	407 (2156), 256 (25 000)
Mo(CO)₆ + NaBr	290–370	Mo(CO)₅Br⁻	406 (2150), 252 (30 000)
Mo(CO)₆ + NaI	333	Mo(CO)₅I⁻	408 (1500), 290 (200)
W(CO)₆ + NaCl	310–380	W(CO)₅Cl⁻	416 (3100), 246 (60 000)
W(CO)₆ + NaBr	333	W(CO)₅Br⁻	416 (3500), 247 (70 000)
W(CO)₆ + NaI	290–370	W(CO)₅I⁻	406 (2750), 333 (1400)

[a] M(CO)₆ in hexane and NaX in water. [b] M(CO)₅X⁻ in water. [c] λ_{max} (nm) and ϵ (M⁻¹ cm⁻¹); see ref 8.

studied in order to achieve an efficient charge separation by a spatial isolation of reactants and products.[1-3] Recently, excited-state electron transfer from a metal complex to an organic acceptor across a macroscopic liquid/liquid interface was also accomplished.[4] Such systems may be useful not only for mechanistic studies but also for synthetic applications. We explored this possibility and selected the photosubstitution of chromium, molybdenum, and tungsten carbonyls by halide anions for the present investigations.[5] While the photolysis was carried out in hexane solutions, the product formation took place in water. This phase-transfer photolysis is based on the different solubilities of reactant and product in both immiscible solvents. The carbonyls dissolve only in the nonpolar alkane, and the substituted carbonyl anions are soluble only in water.

The photolysis was performed in a very simple setup. An optical cell contained both immiscible solutions in two separate layers. In typical experiments the photolysis cell was filled with 2.5 mL of 0.1 M alkali halide in water and 0.5 mL of 5 × 10⁻³ M M(CO)₆ in n-hexane. Both solutions were saturated with argon. Light from a high-pressure lamp (Osram HBO 100 W/2 or Hanovia 1-kW 977 B-1) passed suitable glass or interfence filters, entered the optical cell vertically from the bottom, passed the aqueous solution, and was absorbed by the metal carbonyl in the hexane layer.

The photolysis leads to the well-known dissociation of the hexacarbonyl:[6,7]

$$M(CO)_6 \rightarrow M(CO)_5 + CO$$

The M(CO)₅ fragment recombines with CO or diffuses to the interface where it reacts with halide:

$$M(CO)_5 + X^- \rightarrow M(CO)_5X^-$$
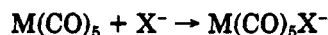
Since M(CO)₅X⁻ does not dissolve in hexane, it accumulates in the aqueous phase.

The progress of the photolysis was monitored by absorption spectroscopy. The optical cell was adjusted to a position which enabled the analyzing light beam of the spectrometer to pass only the aqueous layer. The spectral variations which accompanied the irradiation confirmed the formation of M(CO)₅X⁻ [8] in each experiment (Table

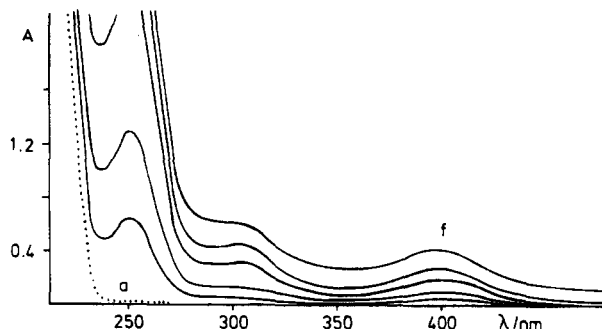(3) Grätzel, M. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; p 435.

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Figure 1. Spectral changes during the photochemical formation of Mo(CO)₅Br⁻ in water in the presence of 0.1 M NaBr by phase-transfer photolysis of 5 × 10⁻³ M Mo(CO)₆ in n-hexane at (a) 0 and (f) 40 min irradiation time, with 290 nm < λ_{irr} < 370 nm and a 1-cm cell.
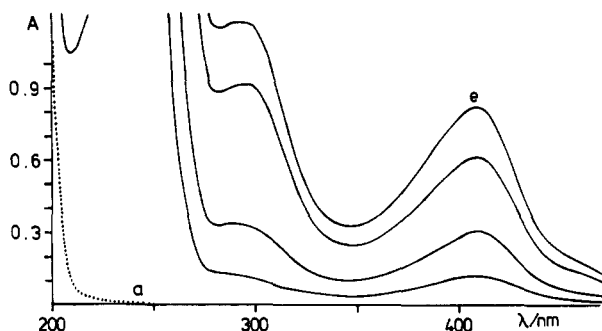

Figure 2. Spectral changes during the photochemical formation of W(CO)₅Cl⁻ in water in the presence of 0.1 M NaCl by phase-transfer photolysis of 5 × 10⁻³ M W(CO)₆ in n-hexane at (a) 0 and (e) 30 min irradiation time, with 310 nm < λ_{irr} < 380 nm and a 1-cm cell.

I). At the beginning, the alkali halide is the only absorbing species in the aqueous phase while the absorption spectrum of M(CO)₅X⁻ develops during the photolysis. Figures 1 and 2 show typical examples. After 30-min irradiation time approximately *30% of W(CO)₆ was converted to W(CO)₅Cl⁻* (spectrum e, Figure 2).

With the arrangement described above, the electronic excitation and the photodissociation of the metal carbonyl occur close to the interface of both layers. This situation favors the product formation since the diffusion of the M(CO)₅ fragment to the interface has to compete with the regeneration of M(CO)₆. However, for synthetic applications it can be a disadvantage that the photolyzing light passes the aqueous layer first since the photoproduct may cause inner-filter effects and can undergo secondary photoreactions. Owing to the rather long lifetime of the M(CO)₅ fragment, a modification of the experimental conditions circumvents these complications. If the irradiating light enters the hexane layer horizontally, the light is immediately absorbed by the hexacarbonyl while the aqueous phase can be kept in the dark.[9] Detrimental inner-filter effects and secondary photolyses are thus avoided. This procedure was successfully applied to the photochemical conversion of M(CO)₆ to M(CO)₅I⁻ with M = Mo and W. However, it must be emphasized that this procedure may not be applicable if a short-lived intermediate or an electronically excited molecule has to reach the interface. Owing to the short lifetime, the electronic excitation must take place very close to the interface. This can be accomplished best when the light hits the interface according to the arrangement described first. Such a simple setup was also used to study the excited-state

(9) Some scattered light also penetrates the aqueous layer.

electron transfer from naphthalene in hexadecane to Co-(NH₃)₆³⁺ in water.[10,11]

Conclusion. In suitable cases the phase-transfer photolysis which features the separation of reactants and products may be developed to a useful synthetic procedure

in organometallic chemistry. Under appropriate conditions inner-filter effects and secondary photolysis which frequently hamper the photolysis in homogeneous solution can be avoided.

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Linear Trimerization of Phenylethyne: Homogeneous Catalysis with *triangulo*-Co₃(μ₃-H)(μ₂-CO)₃(PMe₃)₆

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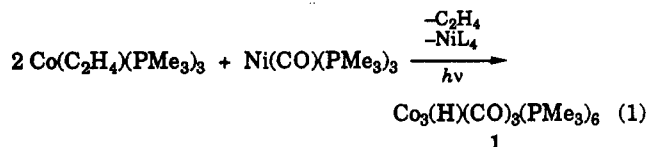Stephan Isringhausen-Bley, Ulrich Flörke, and Hans-Jürgen Haupt

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Summary: Phenylacetylene at 100 °C in the presence of catalytic amounts of the triangulo cluster Co₃(μ₃-H)(μ₂-CO)₃(PMe₃)₆ is transformed into a linear trimer with high regioselectivity and stereoselectivity. Crystals of the new dienyne Ph(PhC≡C)C=CHCH=CHPh in an X-ray structure study are shown to contain molecules in the most stable conformation as expected from MNDO calculations.

Homogeneous catalysis with transition-metal cluster molecules is a promising route to new forms of catalytic activity. While there is no convincing argument against the suspicion that undetected mononuclear intermediates may act as effective catalysts,[1] cluster catalysis continues to supply efficient syntheses that do not succeed without clusters.[2]

Investigating trimethylphosphine complexes of low-valent cobalt and nickel, we found an easy access to molecular clusters of the triangulo type.[3] Irradiation of freely soluble mononuclear compounds of Co(0) and Ni(0) in toluene over 3 h at 80 °C resulted in deposition of the sparingly soluble title compound 1 in 45% yield.[4] Under these conditions no nickel is incorporated (e.g. from Ni(CO)(PMe₃)₃ as a convenient source of carbonyl ligands).

$$2\ Co(C_2H_4)(PMe_3)_3 + Ni(CO)(PMe_3)_3 \xrightarrow[h\nu]{\substack{-C_2H_4 \\ -NiL_4}}$$

$$Co_3(H)(CO)_3(PMe_3)_6 \quad (1)$$

$$\mathbf{1}$$

Table I. Calculated Heats of Formation (kcal mol⁻¹) of Isomers 2A and 2B, Based on Atomic Coordinates Found

method[a]	heat of formation		Δ	RMS[b]
	2A	2B		
AM 1	151.54	152.70	−1.16	0.468
PM 3	151.81	155.33	−3.52	0.389
MNDO	144.48	144.62	−0.14	1.022
MNDO[c]	144.36	145.08	−0.72	1.216

[a] Semiempirical (program packages MOPAC, version 5.0). [b] Deviations of calculated and structurally found molecular geometry. [c] Based on models 2A and 2B:
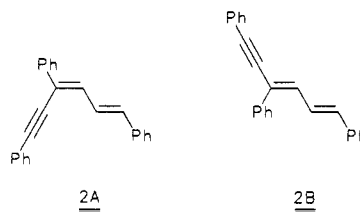
Scheme I. Important Steps in the Linear Trimerization of Phenylethyne[a]
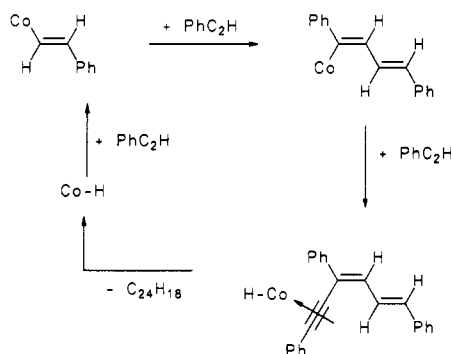
[a] Co stands for a cluster or a mononuclear complex moiety.

Treatment of the D_{3h} cluster 1 (Figure 1) with phenylacetylene for the first time induces a highly selective linear trimerization that does not proceed with mononuclear catalysts, where cyclic oligomers are predominantly formed.[5] As the main product of a typical synthesis[6] (from

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