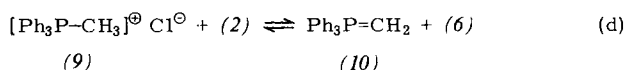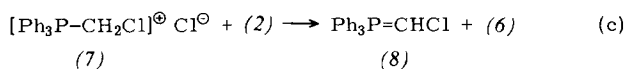determination (calc. 345.2, exp. 335) confirm the existence and the monomeric structure of (3). The mass spectrum contains the molecular peak ($m/e = 344$), accompanied by satellites due to the two chlorine atoms, at an ionization voltage of 13 eV.

Dehydrochlorination of (chloromethyl)triphenylphosphonium chloride (7) with an excess of (2) affords the (chloromethylene)phosphorane (8) whose ^{31}P-NMR signal is observed at -16.9 ppm. In contrast, the reaction according to eq. (d) is found on monitoring by ^{31}P-NMR spectroscopy to lead merely to a broadening of the signals of the starting compounds, which is probably attributable to comparable basicities of the two ylide systems coupled with a fast proton exchange.

$$[Ph_3P-CH_2Cl]^{\oplus} Cl^{\ominus} + (2) \longrightarrow Ph_3P=CHCl + (6) \qquad (c)$$
$$(7) \qquad\qquad\qquad (8)$$

$$[Ph_3P-CH_3]^{\oplus} Cl^{\ominus} + (2) \rightleftharpoons Ph_3P=CH_2 + (6) \qquad (d)$$
$$(9) \qquad\qquad\qquad (10)$$

(Dichloromethylene)triphenylphosphorane (3)

Compounds (5)[4] (3.81 g, 0.01 mol) and (2)[5] (6.7 g, 0.0125 mol) are stirred together at room temperature for 6 h in chlorobenzene (10 ml) and toluene (15 ml). After filtration (glass frit) and washing (3 × 10 ml of toluene) of the residue consisting of (6) and excess (2) the clear filtrate is gently evaporated to dryness in a vacuum. Compound (3) (1.9 g, 55 %) is obtained as a yellow powder which can be redissolved as the monomer in toluene.

[1] A. J. Speziale, G. J. Marco, and K. W. Ratts, J. Am. Chem. Soc. 82, 1260 (1960); A. J. Speziale and K. W. Ratts, ibid. 84, 854 (1962).

[2] R. Rabinowitz and R. Marcus, J. Am. Chem. Soc. 84, 1312 (1962); R. Appel, F. Knoll, W. Michel, W. Morbach, H. D. Wihler, and H. Veltmann, Chem. Ber. 109, 58 (1976); cf. R. Appel, Angew. Chem. 87, 863 (1975); Angew. Chem. Int. Ed. Engl. 14, 801 (1975).

[3] R. Appel, presented at the 25th IUPAC Congress, Jerusalem, July 10, 1975.

[4] R. Appel and W. Morbach, to be published.

[5] F. Ramirez, N. B. Desai, B. Hansen, and McKelvie, J. Am. Chem. Soc. 83, 3539 (1961).

1-Naphthyl Rotation and Metal-Centered Rearrangement in Square-Pyramidal Molybdenum Complexes[1]

By Henri Brunner and Joachim Wachter[*]

In the thioamide complexes $C_5H_5(CO)_2MoSC(R)NR^*$ the Mo atom is a center of asymmetry[2]. Resolvable diastereoisomeric pairs are obtained with $R^* = (S)$-α-phenylethyl[2, 3]. At elevated temperatures the diastereomers undergo mutual interconversion via first-order intramolecular reactions[2, 4].

While the ^{1}H-NMR spectra of complexes with R = H, CH_3, and C_6H_5 show only two C_5H_5 singlets and two CH_3 doublets for each pair of diastereomers[5], twice as many signals are

[*] Prof. Dr. H. Brunner und Dipl.-Chem. J. Wachter
Institut für Chemie der Universität
Universitätsstrasse 31, 8400 Regensburg 2 (Germany)

observed for the compound with R = 1-naphthyl. This is because each Mo configuration (1) and (2) forms two atropisomers (1a)/(1b) and (2a)/(2b) with the 1-naphthyl groups in different orientations[6].

(1a)

(2a)

(1b)

(2b)
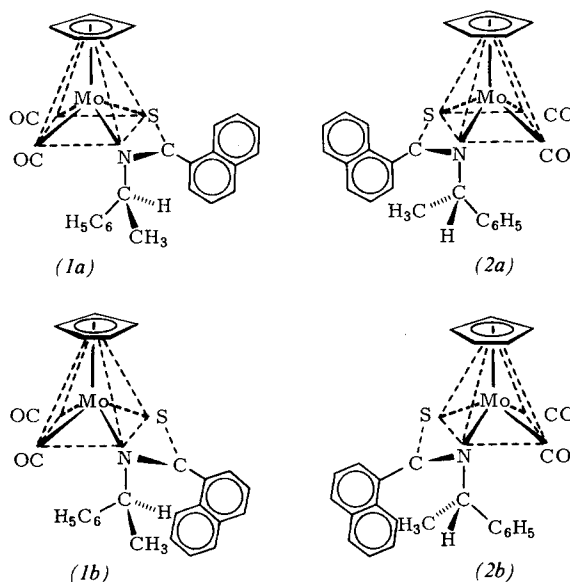
The four isomers arise on reaction of $C_5H_5Mo(CO)_3Cl$ with (S)-$(-)$-N-(α-phenylethyl)-1-naphthothioamide in pyridine at 130°C. The configurational isomers (1) and (2) can be obtained optically pure by fractional crystallization from ether/pentane (10:1)[5]. The sparingly soluble isomer (1) ($[\alpha]_{365}^{20} = -4035°$; 0.3 mg/ml in toluene) gives a ^{1}H-NMR spectrum (90 MHz, $CDCl_3$, -10°C) containing two C_5H_5 signals at $\tau = 4.38$ and 4.46 (isomer ratio $(1a):(1b) = 81:19$). The C_5H_5 signals of the readily soluble isomer (2) ($[\alpha]_{365}^{20} = +3135°$; 0.5 mg/ml in toluene) lie at $\tau = 5.05$ and 5.08 (isomer ratio $(2a):(2b) = 64:36$). The splitting and intensities of the methyl signals resemble those for the C_5H_5 signals.

In $CDCl_3$ solution at 25°C the intensity of the C_5H_5 signals of optically pure (2) gradually diminishes; a concomitant growth of the C_5H_5 signals of (1) progresses up to equilibration at $(1):(2) = 13:87$. The time-dependence of the integrals (51 measurements)[7] affords the rate constants $k_{(1)\to(2)} = 5.36 \times 10^{-5} \pm 0.66 \times 10^{-6}$ s^{-1} and $k_{(2)\to(1)} = 9.19 \times 10^{-6} \pm 0.23 \times 10^{-6}$ s^{-1} as well as the activation energies $\Delta G^{\ddagger}_{(1)\to(2)} = 23.3 \pm 0.1$ kcal/mol and $\Delta G^{\ddagger}_{(2)\to(1)} = 24.3 \pm 0.1$ kcal/mol. The half-life of 184 ± 2 min for the equilibration $(1) \rightleftarrows (2)$ is comparable with the epimerization rates of other thioamide complexes[5]. Hence the observed process is ascribed to a configurational change at the Mo atom.

On heating of (1) or (2) in toluene solution the epimerization equilibrium is rapidly established ($\tau_{1/2}$ at 60°C ca. 1.5 min, extrapolated). The C_5H_5 signals exhibit concomitant broadening. At 63°C the dominant isomer (2) exhibits coalescence; at 80°C the C_5H_5 signals of (1) and (2) are singlets, and the methyl signals doublets. The rate constants $k_{(2a)\to(2b)} = 2.31 \pm 1$ s^{-1} and $k_{(2b)\to(2a)} = 4.32 \pm 1$ s^{-1} and the activation energies $\Delta G^{\ddagger}_{(2a)\to(2b)} = 19.2 \pm 0.3$ kcal/mol and $\Delta G^{\ddagger}_{(2b)\to(2a)} = 18.8 \pm 0.3$ kcal/mol were calculated with the aid of the following parameters[8]: coalescence temperature $T_c = 336 \pm 0.3$°K; linewidth $b_E = 0.6$ Hz; chemical shift $\Delta v = 2.63$ Hz (extrapolated to the coalescense temperature); equilibrium constant $K = 0.55 \pm 0.05$. This process is assigned to 1-naphthyl rotation in (2). The much lower intensity of

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the C_5H_5 signals precludes accurate determination of the values for *(1)*.

In contrast to the 1-naphthyl complexes *(1)/(2)*, the corresponding 2-naphthyl complex does not appear to display any barrier to rotation. Each diastereomer gives only one C_5H_5 signal, which fails to split even on cooling to $-80°C$ in [D_8]-toluene.

[1] Optically Active Transition Metal Complexes, Part 38. We are indebted to *T. Burgemeister* for recording the 90-MHz spectra. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. (S)-(−)-α-Phenylethylamine was kindly supplied by Dynamit Nobel, Troisdorf.—Part 37: *H. Brunner, W. A. Herrmann, and J. Wachter*, J. Organomet. Chem. *107*, C 11 (1976).
[2] *H. Brunner*, Top. Curr. Chem. *56*, 67 (1975).
[3] *H. Brunner* and *W. A. Herrmann*, Chem. Ber. *105*, 3600 (1972).
[4] *H. Brunner* and *W. A. Herrmann*, Chem. Ber. *106*, 632 (1973).
[5] *H. Brunner* and *J. Wachter*, Chem. Ber., in press.
[6] Configurations in reaction scheme are arbitrary.
[7] KIN 2 Program (Fortran); *U. Kölle*, Dissertation, Universität Heidelberg 1969.
[8] *H. Kessler*, Angew. Chem. *82*, 237 (1970); Angew. Chem. Int. Ed. Engl. *9*, 219 (1970).

ABSTRACTS

Reviews

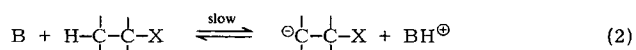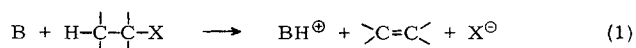Abstracts of selected progress reports and review articles

Persistent carbon-centered radicals are the theme of an article by *D. Griller* and *K. U. Ingold*. The authors suggest this term to symbolize radicals whose lifetime in solution is considerably longer than that of the methyl radical. Under certain experimental conditions the persistence of a radical can be expressed by the rate constant of its decomposition. Triphenylmethyl is a persistent radical; benzyl, vinyl, *tert*-butyl, etc.
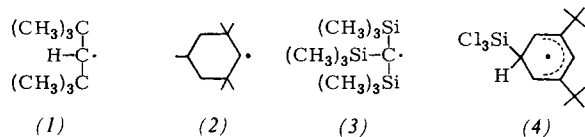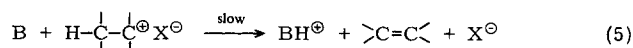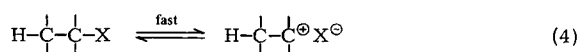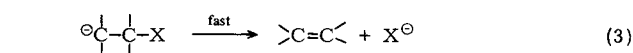

are transient radicals. The thermodynamic stabilization or destabilization of a radical must be considered apart. After it had been shown that steric and non-electronic factors play the principal role in persistence, several persistent radicals were synthesized; examples are *(1)—(4)*. [Persistent Carbon-Centered Radicals. Acc. Chem. Res. *9*, 13—19 (1976); 46 references]

[Rd 845 IE—L]

The distinction between concerted and nonconcerted eliminations is the subject of review by *E. H. Saunders, Jr.* A few years ago there was a certain amount of doubt that concerted reactions, especially E2 eliminations [Eq. (1)], are of frequent occurrence[*]. Instead, it was proposed that eliminations proceed according to the irreversible carbanion mechanism (E1cB)$_I$ [Eq. (2) and (3)] or the ion-pair mechanism (E2)$_{ip}$, [Eq. (4) and (5)]:

$$B + H-\overset{|}{C}-\overset{|}{C}-X \longrightarrow BH^{\oplus} + \hspace{0.2em} >C=C< + X^{\ominus} \tag{1}$$

$$B + H-\overset{|}{C}-\overset{|}{C}-X \underset{}{\overset{slow}{\rightleftharpoons}} \hspace{0.2em} ^{\ominus}\overset{|}{C}-\overset{|}{C}-X + BH^{\oplus} \tag{2}$$

[*] *F. G. Bordwell*, Acc. Chem. Res. *3*, 281 (1970); *5*, 374 (1972).

$$^{\ominus}\overset{|}{C}-\overset{|}{C}-X \xrightarrow{fast} \hspace{0.2em} >C=C< + X^{\ominus} \tag{3}$$

$$H-\overset{|}{C}-\overset{|}{C}-X \underset{}{\overset{fast}{\rightleftharpoons}} H-\overset{|}{C}-\overset{|}{C}^{\oplus}X^{\ominus} \tag{4}$$

$$B + H-\overset{|}{C}-\overset{|}{C}^{\oplus}X^{\ominus} \xrightarrow{slow} BH^{\oplus} + \hspace{0.2em} >C=C< + X^{\ominus} \tag{5}$$

In an E2 process the β H atom is partly detached and the C—X bond partly opened in the transition state of the rate-determining step. It can be concluded from eliminations on β-deuteriated compounds and other experiments that almost all second order eliminations of simple primary and secondary derivatives follow the E2 mechanism. In tertiary and allylic derivatives or α-arylalkyl compounds it is still undecided whether or not the ion-pair mechanism is at issue in many cases. [Distinguishing between Concerted and Nonconcerted Eliminations. Acc. Chem. Res. *9*, 19—25 (1976); 68 references]

[Rd 846 IE—L]

The stereochemical consequences of correlated rotation in propeller molecules are dealt with in an article by *K. Mislow*. Examples are compounds of type *(1)—(3)* ($a \neq b \neq c$), whose substituents contain no stereoisomeric elements. Each rotation of a ring about the B-aryl or CH-aryl bond is accompanied by rotation of the other rings; this coupled motion is referred
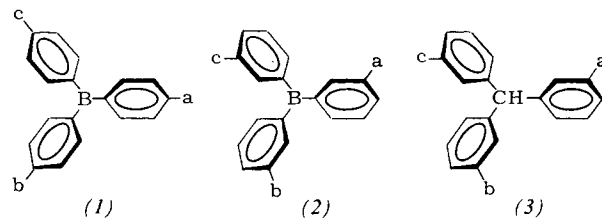
to as correlated rotation. Both the static and the dynamic stereochemistry of these molecules are first discussed. Three further sections of the article are devoted to stereochemical agreements, residual stereoisomerism, and residual stereotopism. [Stereochemical Consequences of Correlated Rotation in Molecular Propellers. Acc. Chem. Res. *9*, 26—33 (1976); 23 references]

[Rd 847 IE—L]

Some new chemical properties of unsaturated C_{18} acids are described by *F. D. Gunstone*. Particularly interesting are the