Transition Metal Complexes of Diazenes, XXV[1]

Photochemical Substitution Reactions of Group VIb Dimetallaheterocycles

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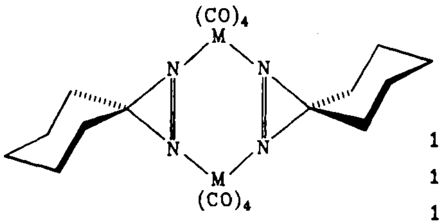
Irradiation of the dimetallacycles $(CO)_4M(\mu\text{-PMD})_2M(CO)_4$ (**1**) (M = Cr, Mo, W; PMD = pentamethylenediazirine) in the presence of bidentate nitrogen ligands L–L (2,2′-bipyridine, 1,4-di-*tert*-butyl-1,4-diazabutadiene, *N,N,N′,N′*-tetramethylethylenediamine) leads to $(L{-}L)M(CO)_4$ (**2**) by cleavage of the metal–diazirine bonds. The quantum yield for the disappearance of the starting compound is 0.056 and 0.0063 when the chromium complex is excited within its metal-centered or CTML band at 368 and 445 nm, respectively. Much lower values, 0.0001 and 0.00009, are found upon CTML excitation of the molybdenum and tungsten complexes, respectively. Contrary to this reaction, irradiation of the chromium complex **1a** in the presence of the bidentate phosphorus ligand dppe, 1,2-bis(diphenylphosphino)ethane, leads to $(CO)_3Cr(\mu\text{-PMD})_2(\mu\text{-dppe})Cr(CO)_3$ (**4a**) by substitution of carbon monoxide. X-ray structural analysis reveals that the planar Cr_2N_4 dimetallacycle present in **1** does not change its geometry upon introduction of the third bridging ligand. UV-VIS reaction spectroscopy and laser flash photolysis indicate that in both reactions CO elimination is the primary photochemical step, followed by monodentate coordination. The successive chelation step occurs at the same chromium atom in the case of nitrogen ligands but at the other atom in the case of the phosphorus ligand. The CTML energy decreases when one and two CO ligands are substituted by triphenylphosphine and dppe, respectively.

Übergangsmetall-Komplexe von Diazenen, XXV[1]. – Photochemische Substitutionsreaktionen von Dimetalla-Heterocyclen der VI. Nebengruppe

Die Belichtung der Dimetallacyclen $(CO)_4M(\mu\text{-PMD})_2M(CO)_4$ (**1**) (M = Cr, Mo, W; PMD = Pentamethylendiazirin) in Gegenwart zweizähniger Stickstoff-Liganden L–L (2,2′-Bipyridin, 1,4-Di-*tert*-butyl-1,4-diazabutadien, *N,N,N′,N′*-Tetramethylethylendiamin) führt unter Spaltung der Metall–Diazirin-Bindungen zu $(L{-}L)M(CO)_4$ (**2**). Die Quantenausbeuten für das Verschwinden des Edukts sind 0.056 und 0.0063 für den Chrom-Komplex bei Anregung des MC- (metal-centered, 368 nm) bzw. des CTML-Zustands (445 nm). Deutlich niedrigere Werte, 0.0001 und 0.00009, ergeben sich bei CTML-Anregung des Molybdän- bzw. des Wolfram-Komplexes. Im Gegensatz zu dieser Reaktion führt die Belichtung des Chrom-Komplexes **1a** in Gegenwart des zweizähnigen Phosphor-Liganden dppe [1,2-Bis(diphenylphosphino)ethan] unter CO-Substitution zu $(CO)_3Cr(\mu\text{-PMD})_2(\mu\text{-dppe})Cr(CO)_3$ (**4a**). Die Röntgenstrukturanalyse ergibt, daß der in **1** vorliegende planare Cr_2N_4-Dimetallacyclus seine Geometrie durch die Einführung des dritten verbrückenden Liganden nicht verändert. Durch UV-VIS-Reaktionsspektroskopie und Blitzlichtphotolyse wird gezeigt, daß der photochemische Primärschritt in beiden Fällen CO-Eliminierung ist, woraufhin einzähnige Koordination folgt. Die nachfolgende Chelatisierung findet im Falle der Stickstoff-Liganden am selben Chrom-Atom, im Falle von dppe dagegen am anderen Metallzentrum statt. Die Energie des CTML-Zustands nimmt bei Substitution eines oder zweier CO-Liganden durch Triphenylphosphan bzw. dppe kontinuierlich ab.

During our investigations of the coordination chemistry of substituted 1,2-diazenes[2] we have employed also the three-membered diazirines as ligands. Because of their special steric and electronic properties they are able to form stable complexes in cases where higher-membered cyclic diazenes give rise to intermediates only. The reactions of diazirines with iron, ruthenium, and titanium carbonyls lead to N=N and C–N bond cleavage[1,3], whereas with group VIb carbonyls the cyclic ligand structure is retained, and complexes with two penta- or tetracarbonylmetal groups bridged by one or two diazirine ligands, respectively, are formed. These latter double-bridged complexes with the ligand spiro[cyclohexane-1,3′-diazirine], pentamethylenediazirine (PMD), possess a planar dimetallacycle[4,5] that gives rise to a significant absorption band in the range of 465 to 475 nm. This absorption was found to have CTML (charge transfer metal to ligand) character, whereas the clearly separated absorption at 350–370 nm has MC (metal-centered) character[6].

In organometallic chemistry there is an increasing interest in the photoreactivity of low-lying CTML states with respect to photosubstitution and photoinduced electron and energy transfer processes[7,8]. We therefore attempted to shift the CTML states of the dimetallacycles **1** to lower energies by introduction of chelating ligands. We report here on photosubstitution reactions of **1** and on their dependence on the ligand and on the energy of the light absorbed.



1a: M = Cr
1b: M = Mo
1c: M = W

Results and Discussion

The complexes $M_2(PMD)_2(CO)_8$ (**1**) were irradiated in solution with a tungsten halogen lamp in the presence of a twofold excess of 2,2′-bipyridine (bpy). With each of the three complexes the reaction resulted in the cleavage of the dimetallacycle yielding the mononuclear complexes $M(CO)_4bpy$:

$$\underset{\mathbf{1}}{M_2(PMD)_2(CO)_8} + 2\,bpy \xrightarrow{h\nu} \underset{\mathbf{2}}{2\,M(CO)_4(bpy)} + 2\,PMD \quad (1)$$

The same result was obtained when 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene (*t*Bu-DAB) or *N,N,N′,N′*-tetramethylethylenediamine (tmeda) was used as a chelating ligand.

Monochromatic irradiation of **1** within the MC band (λ_{exc} = 368 nm for **1a** and 353 nm for **1b** and **1c**) or the CTML band (λ_{exc} = 445 nm) gave the same products in both cases. However, as shown in Table 1, the quantum yields for the disappearance of the starting compound show a marked decrease when going to longer wavelengths. This effect is strongest for **1c** (M = W). Beyond this, quantum yields are decreasing in the order Cr > Mo > W.

Table 1. Quantum yields (mol/*E*) for the disappearance of **1** in reaction (1), measured in toluene

	1a	**1b**	**1c**
Φ_{353}	–	$1.2 \cdot 10^{-2}$	$5.8 \cdot 10^{-3}$
Φ_{368}	$5.6 \cdot 10^{-2}$	–	–
Φ_{445}	$6.3 \cdot 10^{-3}$	$1.1 \cdot 10^{-4}$	$8.8 \cdot 10^{-5}$

Both these effects – dependence of the photoreactivity on wavelength and central metal – have been observed in a similar way for mononuclear complexes of the type $M(CO)_4(R-DAB)$ (M = Cr, Mo, W)[9] and $W(CO)_4L$ (L = bpy, phen)[10]. These compounds are comparable to the complexes **1** with respect to the coordination sphere around their central metals, and like these they have energetically low-lying CTML states. Generally, complexes of this kind exhibit a high photostability because weakening of the π-back donation in the CTML-excited state is largely compensated by its ionic character[8].

However, especially the chromium complex **1a** shows a remarkable reactivity when irradiated within the range of its CTML transition. Whether this is caused by population of a substitution-labile ^{3}MC state or by delocalization of electron density to M–CO antibonding orbitals by "through-space" overlap cannot be decided at present. Balk et al.[9] were able to demonstrate this latter effect for $M(CO)_4$(α-diimine) complexes (M = Cr, Mo, W) by resonance Raman spectroscopy. Similar measurements on **1a** and **1c** did not lead to unambiguous results.

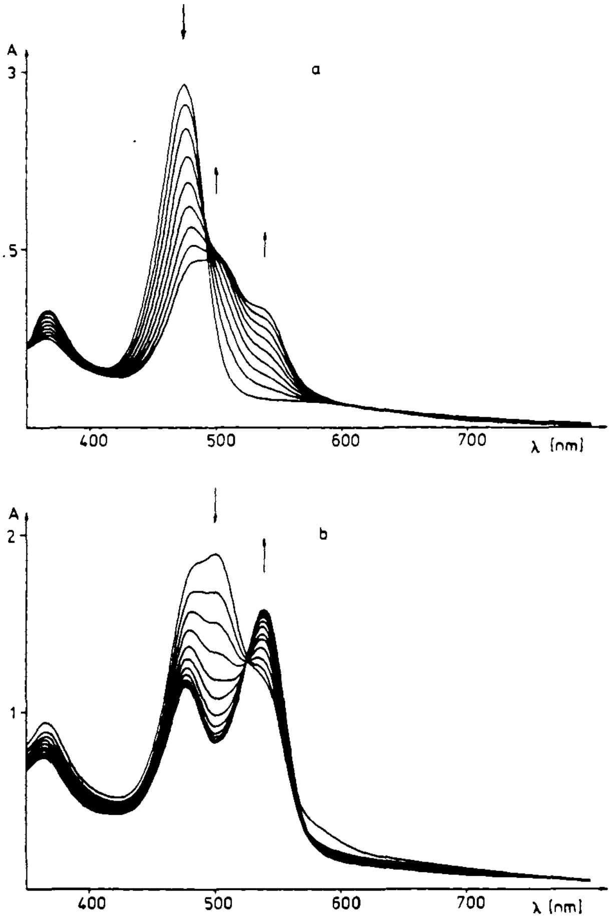


Figure 1. UV-VIS absorption spectral changes of a toluene solution of **1a** and dppe (a) during irradiation (25°C; λ_{exc} = 366 nm; 2.5-min intervals) and (b) while stirring the irradiated solution at 25°C (25-min intervals)

In contrast to the findings shown above, irradiation of **1a** in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) results in the reactions (2) and (3).

$$\underset{\mathbf{1a}}{Cr_2(PMD)_2(CO)_8} + dppe \xrightarrow{h\nu} \underset{\mathbf{3a}}{Cr_2(PMD)_2(CO)_7dppe} + CO \quad (2)$$

$$\mathbf{3a} \longrightarrow \underset{\mathbf{4a}}{Cr_2(PMD)_2(dppe)(CO)_6} + CO \quad (3)$$

The reaction sequence can be followed by UV-VIS spectroscopy (Figure 1). As the intensities for the absorptions of the starting compound at 367 and 475 nm decrease with increasing irradiation time, new bands at 505 and 538 nm appear (Figure 1a). When the irradiated solution is stirred under exclusion of light, the 505-nm absorption decreases while the absorbance at 538 nm experiences an additional increase (Figure 1b). We therefore assign the latter band to the product **4a**, the former to the intermediate **3a**. The latter is produced in the first, photochemical reaction (eq. 2) and contains a monodentate dppe ligand. The second, thermal step (eq. 3) leads to the triple-bridged complex **4a** (Figure 3). The same reaction sequence is observed with selective MC- or CTML excitation. Photochemical reaction of **1a** with triphenylphosphine yields the monosubstitution product $Cr_2(PMD)_2(CO)_7PPh_3$ (**5a**). Its UV-VIS spectrum (Figure 2) is in good agreement with that of the intermediate **3a** (Figure 1).

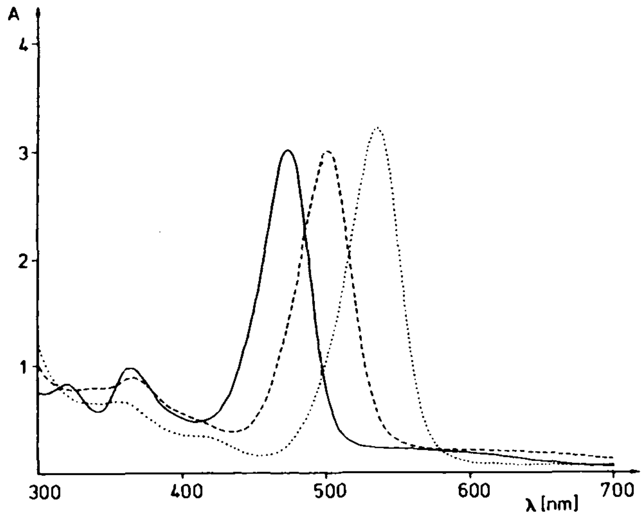


Figure 2. UV-VIS absorption spectra of **1a** (———), **4a** (·····) and **5a** (— — —) in toluene

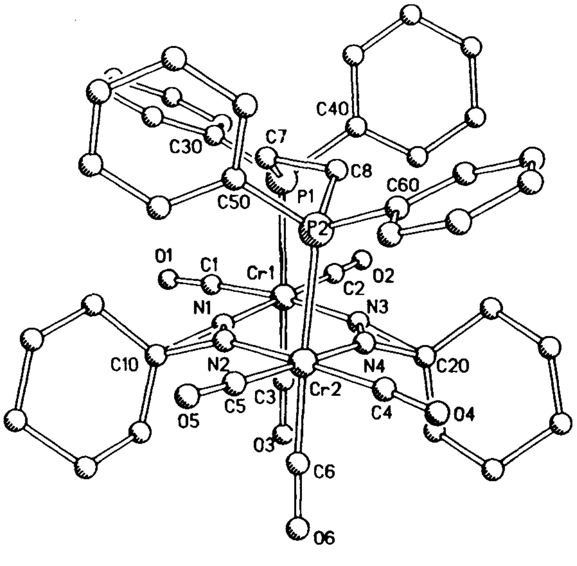


Figure 3. Molecular structure of **4a**

The UV-VIS spectra of **4a** and **5a** (Figure 2) exhibit the typical pattern of the chromophor M(RN=NR)M[6]. In agreement with their MC character the short wavelength absorptions at 363 nm (**4a**) and 368 nm (**5a**) are hardly shifted in comparison with the parent compound **1a** (367 nm). The increasing red shift of the long wavelength absorption with increasing extent of substitution of the dimetallacycle (**1a**, **5a**, and **4a**) confirms the CT character of this band.

X-ray analysis data of **4a** are summarized in Tables 2–4; the molecular structure is shown in Figure 3.

Table 2. Crystallographic data of **4a**[a]

Chemical formula $C_{44}H_{44}Cr_2N_4O_6P_2$, molecular mass 890.80
crystal dimensions 0.70 • 0.30 • 0.20 mm^3, colour green
a = 1143.8(2), b = 1949.2(2), c = 2011.6(3) pm; β = 96.86(1)°
V = $4.453 \cdot 10^9$ pm^3, calcd. density 1.33 $g \cdot cm^{-3}$
space group $P2_1/c$, Z = 4
diffract. Nicolet R3m/V, radiation Mo-K_α (71.073 pm)
reflections measured 9547, unique reflections 7828,
observed reflections 4677 [$F_0 > 6\sigma(F_0)$]
number of parameters 524
R = 6.8, R_w = 5.0 ($w = 1/\sigma^2$)
residual electron density $0.39 \cdot 10^{-6}$ e/pm^3
no absorption correction

[a] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53709, the names of the authors, and the journal citation.

Table 3. Selected bond distances (pm) and -angles (°) of **4a**

bond distances		bond angles	
Cr(1)-P(1)	241.9(2)	N(1)-Cr(1)-N(3)	91.8(3)
Cr(2)-P(2)	241.4(2)	N(2)-Cr(2)-N(4)	81.0(2)
Cr(1)-N(1)	198.3(5)	P(1)-Cr(1)-N(1)	90.6(2)
Cr(1)-N(3)	202.7(6)	P(2)-Cr(2)-N(4)	90.3(2)
Cr(2)-N(4)	198.8(5)	Cr(1)-N(1)-N(2)	141.4(5)
Cr(2)-N(2)	201.8(6)	Cr(1)-N(3)-N(4)	137.7(4)
Cr(1)-C(1)	185.1(9)	Cr(2)-N(2)-N(1)	137.4(4)
Cr(1)-C(2)	186.7(7)	Cr(2)-N(4)-N(3)	141.1(5)
Cr(1)-C(3)	187.0(8)	N(1)-N(2)-C(10)	64.0(4)
Cr(2)-C(4)	183.9(8)	N(2)-N(1)-C(10)	65.3(4)
Cr(2)-C(5)	186.3(7)	N(3)-N(4)-C(20)	64.4(4)
Cr(2)-C(6)	189.2(8)	N(4)-N(3)-C(20)	65.1(4)
N(1)-N(2)	127.0(8)	N(1)-C(10)-N(2)	50.7(4)
N(3)-N(4)	126.7(8)	N(3)-C(20)-N(4)	50.5(4)
N(1)-C(10)	147.6(9)		
N(2)-C(10)	149.2(9)		
N(3)-C(20)	148.2(9)		
N(4)-C(20)	149.0(9)		

As in the parent compound **1a**[5] the six-membered Cr_2N_4 cycle in **4a** is planar – the bridging coordination of dppe has no impact on the basic geometry of the dimetallacycle. Contrary to that, replacement of the bridging diazirines in **1** by the four-membered 1,2-diazetine induces formation of a nonplanar dimetallacycle in $W_2(TMD)_2(CO)_8$ (TMD =

3,3,4,4-tetramethyl-1,2-diazetine)[11]. The N=N bond distance of the diazirine ligand in **4a** (127 pm) is slightly elongated compared to noncoordinated dimethyldiazirine (123 pm)[12] and corresponds to the value of 126 pm for the unsubstituted dimetallacycle **1a**[5].

In order to gain more information about the initial photochemical process, laser flash photolysis measurements were performed on **1a**. In several solvents at room temperature a transient is formed within the pulse width of 15 ns (λ_{exc} = 353 nm). The transient exhibits a major maximum at about 520 nm, a minor one around 410 nm, and a bleaching in the 430–490 nm range, i.e. at the CTML band. An example is shown in Figure 4.

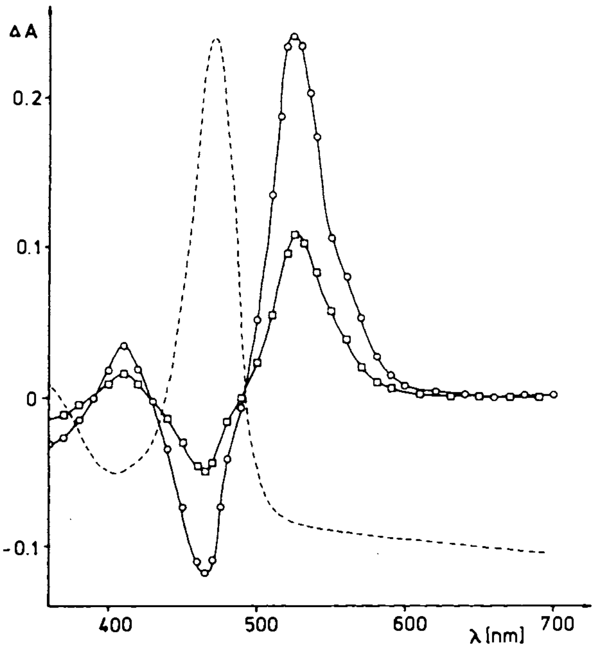


Figure 4. Transient absorption spectrum of **1a** in CO-saturated toluene at 25 °C measured 0.1 µs (○) and 1 ms (□) after the pulse, λ_{exc} = 353 nm A_{470} = 2 in 1 cm; the dotted line refers to the ground-state absorption spectrum

The transient absorption spectrum is virtually identical in toluene and dichloromethane and the same in either Ar- or CO-saturated solution. In the other solvents used (*n*-pentane, benzene, acetone, dioxane, acetonitrile) it was found that the maximum is very similar (Table 4).

While the solvent has no discernible influence on the transient absorption spectrum, it has a significant effect on the decay kinetics which also strongly depend on the presence or absence of CO. In acetone and dioxane the transient remains for several seconds, irrespective of CO or Ar saturation, whereas in the other solvents CO induces a shorter half-life. Generally, the absorbance at 522 nm and the bleaching at 455 nm disappear similarly, and the decay obeys neither a pure first- nor a second-order rate law. For this reason we used the half-life ($t_{1/2}$) as a kinetic measure of the decay. In Ar-saturated solution $t_{1/2}$ decreases in the order acetone, dichloromethane, toluene, *n*-pentane (Table 4).

Table 4. Minima and maxima of the transient absorption spectrum and half-lives for decay of **1a** in Ar- and CO-saturated solution[a]

Solvent	λ_{min} [nm]	λ_{max} [nm]	$t_{1/2}$ [s] Ar	CO
n-Pentane	[b]	525	≥0.3	≈0.01
Toluene	465	523	≥1	≤0.0001[c]
Benzene	[b]	525	≥1	≤0.002
Dioxane	[b]	525	>1	>1
Dichloromethane	455	522	≥1	≥0.001[c]
Acetone	455	520	>2	>1
Acetonitrile	450	515	≥1	≥0.1

[a] At 25 °C using λ_{exc} = 353 nm; virtually the same decay kinetics were obtained at 530 nm using λ_{exc} = 532 nm. — [b] Observation of bleaching was not possible due to larger A_{470} (3–4; 1–2 in the other cases). — [c] Same value obtained from bleaching.

The decay of the transient in CO-saturated toluene, measured both at 520 and 460 nm, is significantly faster than in the absence of CO, its $t_{1/2}$ value is about 0.1 ms (Figures 5a and b). The $t_{1/2}$ values in CO-saturated acetone, dichloromethane, and *n*-pentane are > 1 s, ≥ 1 ms and ≈ 10 ms, respectively. In addition to the fast component there is also a slower one; the contribution of both components is approximately 60 and 40%, respectively. This decay pattern is the same when **1a** is excited at 532 nm. An example of the decay at 530 nm is shown in Figures 5c and d. When analyzed by first-order kinetics, the lifetimes are about 60 µs and 3 ms. Similar values (40 µs and 4 ms) were measured in benzene, while in CO-saturated dichloromethane and *n*-pentane one of the two components dominates.

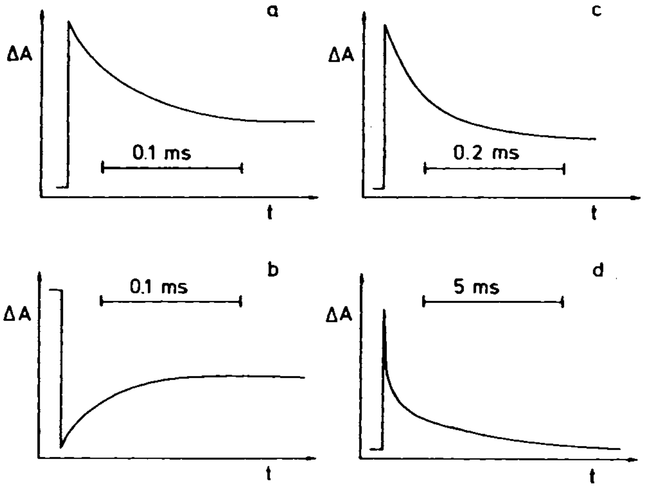


Figure 5. Transient optical density of **1a** in CO-saturated toluene versus time after laser pulse excitation; (a) absorption at 523 nm and (b) bleaching at 465 nm, λ_{exc} = 353 nm; (c) and (d) absorption at 530 nm, λ_{exc} = 532 nm; the magnitude of ΔA corresponds to Figure 4

Since the absorption spectrum is identical for the two components (Figure 4), we conclude that a consecutive decay of the same transient occurs rather than formation of a second transient. The results are explained by attributing the transient of **1a** to a solvent-coordinated intermediate $Cr_2(PMD)_2(CO)_7(Solv.)$ (**6a**). From the kinetic and spectroscopic observations it follows that **6a** is formed within 20 ns. Its stability can considerably be increased by addition of a better ligand, e.g. acetone (Table 4). For example, in CO-saturated toluene $t_{1/2}$ is increased by a factor of more than 100 by addition of about 1% acetone. Under Ar the dimetallacycle decomposes to a colourless product, as evidenced by the bleaching of the reaction mixture.

There is no experimental evidence for a reversible cleavage of one M–N bond in the dimetallacycle. Thus, the initial photochemical process is CO elimination. This also explains the observation that $t_{1/2}$ is diminished in Ar-saturated toluene on repeated flashing of the same sealed volume and that it is restored to its initial value after merely fresh degassing with Ar. Obviously, the decay kinetics of **6a** in Ar-saturated solution are influenced by traces of CO. Since the starting compound **1a** is recovered completely in CO-saturated solution, as demonstrated by the complete recovery of A_{460}, it can be assumed that both components in the transient decay kinetics in CO-saturated solution (Figures 5c and d) are due to recombination reactions with CO. A decision as to whether or not a solvent-free intermediate could be responsible for the fast process is not yet possible.

The assumption of a dissociative mechanism is further supported by the fact that the quantum yields for the disappearance of **1a** (measured in N_2-saturated toluene solution) are only slightly increased by an excess of phosphine ligand. Thus, without any ligand $\Phi_{368} = 4.6 \cdot 10^{-2}$ was measured, whereas in the presence of a tenfold excess of dppe Φ_{368} is $5.3 \cdot 10^{-2}$.

Under the conditions of continuous irradiation of **1a** similar observations as in laser flash photolysis are made. Thus, in CO-saturated solution the bleaching is only 7% of that measured in Ar-saturated solution. This, too, shows that at low CO concentrations **6a** predominantly decomposes to a colourless product. Irradiation of **1a** at −60°C (λ_{exc} = 366 nm) under Ar or CO causes the same changes in the UV-VIS spectrum as observed by the laser excitation (Figure 4). Warming up the solution irradiated under Ar to −20°C entails complete disappearance of the 520-nm absorption without reformation of the starting material **1a**.

From this results we propose a mechanism that can explain both photoreactions of **1a**, substitution of CO by phosphines, and cleavage of the metal–diazirine bonds by bpy and other nitrogen donors (Scheme 1).

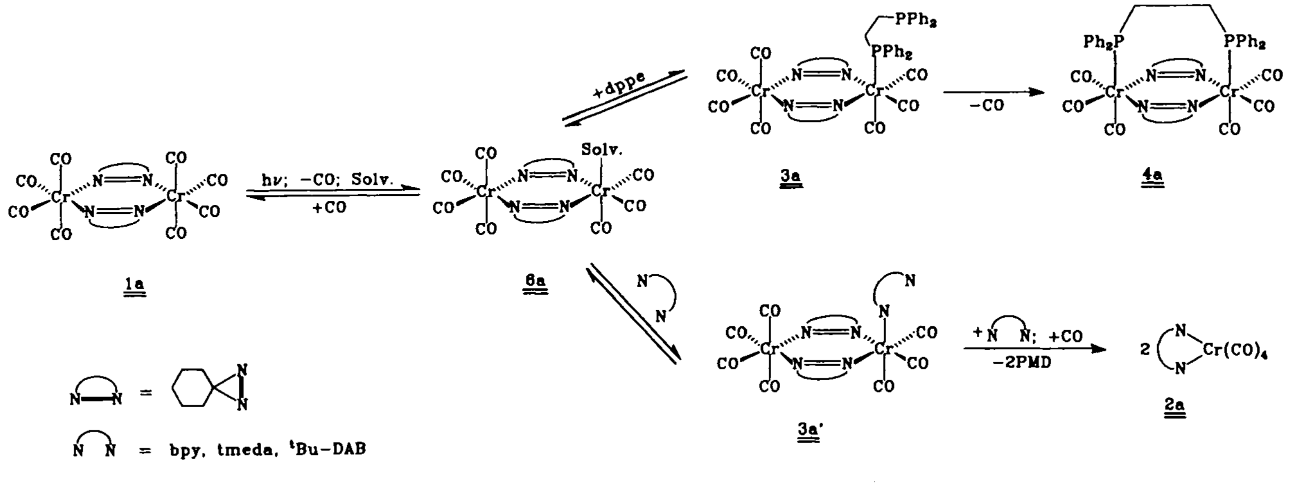
The first step consists of the photochemical elimination of one CO ligand. The resulting coordinatively unsaturated species immediately forms the intermediate **6a** by coordination of a solvent molecule. It can be observed by UV-VIS spectroscopy during laser flash photolysis as well as by continuous irradiation at low temperatures.

When dppe is present, the triple-bridged product **4a** is formed via the monodentate intermediate **3a**. It is very likely that also in the presence of the nitrogen ligands bpy, *t*Bu-DAB, and tmeda the second reaction step affords an analogous intermediate **3a'**. However, opposite to the dppe reaction, there is no spectroscopic indication for this intermediate, although bidentate nitrogen ligands coordinating in a monodentate fashion have been observed in photochemical and thermal reactions of group VIb hexacarbonyls with substituted and unsubstituted bipyridines[13], dipyridylalkanes[14], 1,4-diazabutadienes[15], and ethylenediamine[16].

Apparently, the subsequent chelation step of **3a'** is too fast compared with that of **3a**, where the second metal atom is attacked by the phosphorus ligand. Whether steric or electronic properties are responsible for the different reactivity of **3a** and **3a'** cannot be decided at the present. It may be speculated that the transition state for chelation at the same metal center is too crowded in the case of the reaction **3a** ⟶ **4a** due to the presence of the two phenyl groups at the ligating phosphorus atom. In the case of **3a'** only two methyl groups or one tertiary butyl group are present at the ligating nitrogen atom, causing far less steric hindrance[17]. Formation of the final product **2a** occurs by cleavage of both metal–diazirine bonds.

In addition to the photochemical processes shown in this paper substitution reactions of **1a** and **1b** can also be induced by electrochemical reduction following an ETC (electron transfer catalysis) mechanism[18].

Scheme 1. Proposed mechanism for the reations of **1a** described in the text



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Experimental

All manipulations with metal carbonyls were carried out under nitrogen. Dichloromethane was freshly destilled from CaH_2, hydrocarbon solvents and THF from sodium. Silica gel (Merck, 230–400 mesh) for chromatography was degassed and kept under nitrogen. Complexes **1**[6] and *t*Bu-DAB[19] were prepared and purified according to the literature; bpy, PPh_3 (Fluka), dppe (Strem), and tmeda (Aldrich) were used as purchased without further purification.

All reaction mixtures were evaporated to dryness (ca. 5 Torr at 25°C) and redissolved in a minimum amount of eluent prior to chromatography.

Polychromatic irradiations were performed with an Osram Xenophot HLX 150-W lamp in a Pyrex glass apparatus, monochromatic irradiations with an Osram HBO 500-W lamp and a Kratos Model GM 252 monochromator using a 1-cm quartz cuvette as reaction vessel.

IR-spectra: Perkin-Elmer model 983 spectrophotometer. – UV-VIS spectra: Shimadzu model 260 spectrophotometer. – NMR spectra: JEOL-GX 270 instrument. – A Hellma low-temperature 1-cm quartz cuvette was used for measuring temperature-dependent UV-VIS spectra. – Quantum yields were measured with an electronically integrating actinometer[20] employing an Osram HBO super pressure mercury 500-W lamp as a light source and a Kratos model GM 252 monochromator. Light intensities were measured by ferri oxalate actinometry[21]; typical light intensities were in the range of $3 \cdot 10^{-7} - 10^{-6}$ *E*/min.

The laser flash photolysis experiments were carried out in Mülheim/Ruhr, using a set-up as described elsewhere[22]. In addition, a second transient digitizer (Tektronix 390AD) was used for detection of the long-lived transient signals. With solutions of **1a** we found that even the small intensity of the analyzing light beam has a disturbing influence on the transient decay kinetics. To avoid this, we placed neutral density filters or a 530-nm interference filter between the xenon lamp and the cuvette. All measurements were carried out at 25°C.

Photoreaction of Complexes $M_2(PMD)_2(CO)_8$ *(***1***) with bpy:* 220 mg (0.40 mmol) of $Cr_2(PMD)_2(CO)_8$ (**1a**), 225 mg (0.40 mmol) of $Mo_2(PMD)_2(CO)_8$ (**1b**), or 325 mg (0.40 mmol) of $W_2(PMD)_2(CO)_8$ (**1c**) together with 125 mg (0.80 mmol) of bpy is irradiated in 200 ml of toluene. The reaction is assumed to be completed when there are no more changes observable in the IR spectrum, which is the case after 6, 18, and 36 h for **1a**, **1b**, and **1c**, respectively. The further treatment of the reaction mixture varies with the different starting compounds:

1a: During the irradiation precipitation of voluminous bright orange crystals occurs. They are collected by filtration. Cooling the filtrate to −20°C yields more precipitate. The combined precipitates are washed with *n*-hexane and dried in vacuo; yield 185 mg (72%). The product was identified as $Cr(CO)_4$bpy by elementary analysis, mass spectrometry, and by its ν_{CO} bands in the IR spectrum[23].

1b: Chromatography of the reaction mixture on silica gel with *n*-hexane/toluene (1:1) gives first a greenish-yellow band of unreacted **1b**. Elution with increasing ratios of toluene/*n*-hexane developes an orange-red product band; yield 226 mg (78%). This product was identified as $Mo(CO)_4$bpy by elementary analysis, mass spectrometry, and by its ν_{CO} bands in the IR spectrum[23].

1c: As for **1b**. Maroon-red crystals; yield 206 mg (57%). Identified as $W(CO)_4$bpy.

Photoreaction of $Cr_2(PMD)_2(CO)_8$ (**1a**) *with tmeda:* A solution of 200 mg (0.37 mmol) of **1a** and 85 mg (0.74 mmol) of tmeda in 200 ml of toluene is irradiated for 4 h; the reaction is completed as indicated by IR. Chromatography with *n*-hexane/toluene (1:1) gives first a small band of unreacted **1a**. Elution with *n*-hexane/THF (1:2) yields the major deep yellow band. The product is identified as $Cr(CO)_4$tmeda by elementary analysis, mass spectrometry, and by its ν_{CO} bands in the IR spectrum[24].

Photoreaction of **1a** *with tBu-DAB:* A $5 \cdot 10^{-5}$ M toluene solution of **1a** containing $5 \cdot 10^{-4}$ M *t*Bu-DAB is irradiated in a 1-cm quartz cuvette (λ_{exc} = 368 nm). After 30 min of irradiation the UV-VIS spectrum shows a new absorption at 566 nm and a weaker one at 392 nm; this spectrum is identical with that of authentic $Cr(CO)_4$*t*Bu-DAB.

[1,2-Bis(diphenylphosphino)ethane]hexacarbonylbis(pentamethylenediazirine)dichromium(0) (**4a**): A solution of 0.50 g (0.91 mmol) of **1a** and 0.73 g (1.83 mmol) of dppe in 350 ml of toluene is irradiated for 5 h. Chromatography with *n*-hexane/dichloromethane (3:1) gives first a greenish-yellow band of unreacted **1a**. With increasing ratios of dichloromethane/*n*-hexane the major intensive violet band is developed. The solvent is evaporated and the residue dissolved in 30–40 ml of dichloromethane. Above the remaining solution, which is transferred into a narrow Schlenk tube, a layer of 150 ml of *n*-hexane is placed cautiously. Cooling to −20°C for several days leads to precipitation of dark green crystals of **4a**; yield 295 mg (36%). One of these crystals was used for X-ray analysis. – IR (ν_{CO}, cm^{-1}, CH_2Cl_2): 1966 s, 1917 vs, 1888 m, 1858 s, 1839 m (sh). – UV-VIS (nm, CH_2Cl_2) ($\varepsilon \cdot 10^3$): 363 (10.4), 410 sh, 535 (49.5). – ^{31}P-NMR (ppm vs. 85% H_3PO_4): 27.6.

$C_{44}H_{44}Cr_2N_4O_6P_2$ (890.8)	Calcd.	C 59.33	H 4.98	N 6.29
	Found	C 59.49	H 5.11	N 5.95

Table 5. Selected atomic coordinates ($\cdot 10^4$) and equivalent isotropic thermal parameters ($pm^2 \cdot 10^{-1}$) for **4a**

	x	y	z	U(eq)
Cr(1)	1999(1)	5377(1)	3609(1)	35(1)
Cr(2)	3215(1)	5460(1)	1661(1)	36(1)
P(1)	1928(2)	4141(1)	3508(1)	33(1)
P(2)	3345(2)	4224(1)	1646(1)	36(1)
N(1)	1365(5)	5476(3)	2652(3)	38(2)
N(2)	1687(5)	5467(3)	2070(3)	34(2)
N(3)	3533(5)	5440(3)	3203(3)	35(2)
N(4)	3862(5)	5469(3)	2624(3)	34(2)
C(7)	2029(6)	3793(4)	2669(3)	38(3)
C(8)	3287(6)	3809(4)	2463(3)	39(3)
C(1)	493(7)	5407(4)	3858(4)	50(3)
O(1)	-427(5)	5451(3)	4040(3)	70(3)
C(2)	2599(7)	5289(4)	4510(4)	46(3)
O(2)	2890(5)	5245(3)	5072(3)	75(3)
C(3)	2017(8)	6324(4)	3759(4)	55(3)
O(3)	1999(7)	6899(3)	3875(3)	97(3)
C(4)	4678(7)	5525(4)	1373(3)	46(3)
O(4)	5578(5)	5610(3)	1168(3)	72(3)
C(5)	2482(7)	5467(5)	783(4)	54(3)
O(5)	2033(5)	5486(4)	244(3)	87(3)
C(6)	3232(8)	6429(4)	1617(4)	58(3)
O(6)	3288(7)	7005(3)	1558(4)	105(4)

Heptacarbonylbis(pentamethylenediazirine)(triphenylphosphine)dichromium(0) (**5a**): A solution of 0.25 g (0.46 mmol) of **1a** and 0.48 g (1.83 mmol) of PPh_3 in 200 ml of toluene is irradiated and worked up as above. Dark green crystals; yield 185 mg (51%). – IR (ν_{CO}, cm^{-1}, CH_2Cl_2): 2022 s, 1946 s (sh), 1930 vs, 1879 s, 1850 m (sh). – UV-VIS (nm, CH_2Cl_2) ($\varepsilon \cdot 10^3$): 368 (10.4), 403 sh, 503 (33.2). – ^{31}P-NMR (ppm, vs. 85% H_3PO_4): 48.2.

$C_{37}H_{35}Cr_2N_4O_7P$ (782.7)	Calcd.	C 56.78	H 4.51	N 7.16
	Found	C 57.87	H 4.87	N 6.87

CAS Registry Numbers

1a: 75194-41-1 / **1b**: 58146-84-2 / **1c**: 58146-85-3 / **4a**: 121373-88-4 / **5a**: 121373-89-5 / bpy: 366-18-7 / *t*Bu-DAB: 30834-74-3 / tmeda: 110-18-9 / dppe: 1663-45-2 / PPh_3: 603-35-0 / $Cr(CO)_4$bpy: 15668-63-0 / $Mo(CO)_4$bpy: 15668-64-1 / $W(CO)_4$bpy: 15668-66-3 / $Cr(CO)_4$tmeda: 21136-10-7 / $Cr(CO)_4$*t*Bu-DAB: 67033-21-0

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[1] XXIV. Mitteilung: G. Avar, W. Rüsseler, H. Kisch, *Z. Naturforsch., Teil B,* **42** (1987) 1441.

[2] A. Albini, H. Kisch, *Top. Current Chem.* **65** (1976) 105.

[3] A. Albini, H. Kisch, *J. Organomet. Chem.* **94** (1975) 75; P. Mastropasqua, A. Riemer, H. Kisch, C. Krüger, *ibid.* **148** (1978) C 40.

[4] W. Beck, W. Danzer, *Z. Naturforsch., Teil B,* **30** (1975) 716.

[5] W. P. Fehlhammer, A. Liu, unpublished results.

[6] R. Battaglia, H. Matthäus, H. Kisch, *J. Organomet. Chem.* **193** (1980) 57.

[7] K. Kalyanasundaram, *Coord. Chem. Rev.* **46** (1982) 159.

[8] H. K. van Dijk, P. C. Servaas, D. J. Stufkens, A. Oskam, *Inorg. Chim. Acta* **24** (1985) 4494, and references therein.

[9] R. W. Balk, T. Snoeck, D. J. Stufkens, A. Oskam, *Inorg. Chem.* **19** (1980) 3015.

[10] M. S. Wrighton, D. L. Morse, *J. Organomet. Chem.* **97** (1975) 405.

[11] B. Bovio, *J. Organomet. Chem.* **241** (1983) 363; B. Albini and H. Kisch, *Z. Naturforsch., Teil B,* **37** (1982) 468.

[12] J. E. Wollrab, L. H. Scharpen, D. P. Ames, *J. Chem. Phys.* **49** (1968) 2405.

[13] R. J. Kazlauskas, M. S. Wrighton, *J. Am. Chem. Soc.* **104** (1982) 5784; M. J. Schadt, A. J. Lees, *Inorg. Chem.*, **25** (1986) 672.

[14] D. E. Marx, A. J. Lees, *Organometallics* **5** (1986) 2072.

[15] L. H. Staal, D. J. Stufkens, A. Oskam, *Inorg. Chim. Acta* **26** (1987) 255; M. J. Schadt, N. J. Gresalfi, A. J. Lees, *Inorg. Chem.* **24** (1985) 2942.

[16] D. E. Marx, A. J. Lees, *Inorg. Chem.* **26** (1986) 2254.

[17] By comparison with the work on the chelation reaction of $(CO)_5M(L-L)$ (M = Cr, Mo, W; L – L = bidentate phosphorus or nitrogen ligand) it seems likely that **3a'** reacts by an associative mechanism; L. Chan, A. J. Lees, *J. Chem. Soc., Dalton Trans.* **1987**, 513; J. A. Connor, J. P. Day, E. M. Jones, G. K. McEwen, *ibid.* **1973**, 347; J. A. Connor, G. A. Hudson, *J. Organomet. Chem.* **73** (1974) 351.

[18] P. Holzmeier, H. Kisch, J. K. Kochi, unpublished results.

[19] L. H. Staal, L. H. Polm, K. Vrieze, F. Ploeger, C. H. Stam, *Inorg. Chem.* **20** (1981) 3590.

[20] W. Amrein, J. Gloor, K. Schaffner, *Chimia* **28** (1974) 185.

[21] C. A. Parker, *Proc. Roy. Soc. Ser.* **220** (1953) 104; C. G. Hatchard, C. A. Parker, *ibid.* **235** (1956) 518.

[22] A. Fernandez, H. Görner, H. Kisch, *Chem. Ber.* **118** (1985) 1936.

[23] M. H. B. Stiddard, *J. Chem. Soc.* **1962**, 4712.

[24] R. T. Jernigan, R. A. Brown, G. R. Dobson, *J. Coord. Chem.* **2** (1972) 47.

[64/89]