dioxide and L_2Pt^0 on photolysis.[1,37] There are, however, some very significant differences. On the basis of model reactions (eqs 1 and 2),[38] it is clear that the thermodynamics of glycolate cycloreversion should be much less favorable than for oxalate cycloreversion. In fact, glycolate photoreversion may result in a significant net storage of photochemical energy. In addition, alteration of the glycol substituents provides a means to increase complex solubility and to probe details of the reaction photochemistry, options that are simply not possible with metal oxalates.

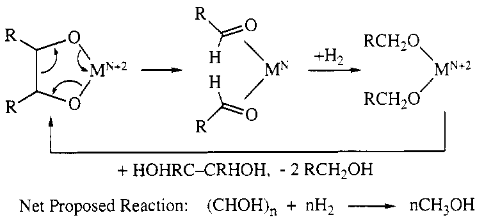
$$HOCH_2CH_2OH \rightarrow 2HCHO + H_2 \quad \Delta G^\circ = +24.5\ \text{kcal/mol} \tag{1}$$

$$HO_2CCO_2H \rightarrow 2CO_2 + H_2 \quad \Delta G^\circ = -21.7\ \text{kcal/mol} \tag{2}$$

In the course of our trapping studies, we discovered that dihydride monomer **3**, which has been reported to readily lose hydrogen to form the neutral dihydride dimer $(dppe)Pt(\mu\text{-}H)_2Pt(dppe)$[39,40] (eq 3), actually exists in facile, nearly thermoneutral equilibrium with the dimer under hydrogen: $K_{eq} = 1.7$ at 22 °C (^{1}H NMR, THF-d_8).

$$2(dppe)PtH_2 \rightleftharpoons (dppe)Pt(\mu\text{-}H)_2Pt(dppe) + H_2 \tag{3}$$

The formation of these platinum hydrides suggests that it might be possible to convert the observed oxidative cleavage[41] into a reductive cleavage. This could serve as a basis for the development of a catalytic cycle for effecting the hydrocracking of carbohydrate C–C bonds (eq 4). In fact, no aldehyde or ketone hydrogenation products were observed in photolyses of the platinum glycolate complexes under hydrogen, even when substantial amounts of the platinum hydrides were present. We therefore carried out



(4)

Net Proposed Reaction: $(CHOH)_n + nH_2 \longrightarrow nCH_3OH$

the photolysis of carbohydrate model complex **1g** in the presence of the known aldehyde hydrogenation catalyst $(PPh_3)_4RuH_2$[42,43] (0.15 equiv, THF, 1.5 atm of H_2). The sole organic product observed (Scheme II) was 1,2-isopropylideneglycerol (**5**; 84% by GC, identified by ^{1}H NMR spectroscopy and comparison of the GC–MS pattern with that of an authentic sample).[44] Glycerol **5** is postulated to originate from initial photolytic cleavage of the dioxaplatinacycle **1g** to give 2 equiv of 2,3-isopropylideneglyceraldehyde, which is subsequently hydrogenated by the Ru catalyst. Studies are now being directed at the chemistry of new metal glycolate systems, with the goal of finding a single metal system capable of catalytically effecting the complete net reaction shown in eq 4 under thermal conditions.

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Supplementary Material Available: Synthetic, spectroscopic, and analytical details for **1a–g**, additional experimental details of the photolyses, and a figure giving the UV–vis spectra of **1a,e** (9 pages). Ordering information is given on any current masthead page.

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[37] Blake, D. M.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5359–5364.

[38] Although the model reactions do not accurately correspond to the reactions of interest, the binding strengths of the two ligands to Pt(II) should not be sufficiently different to alter the conclusion that glycolate cycloreversion should be much less favorable than oxalate cycloreversion.

[39] Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1554–1556.

[40] Scrivanti, A.; Campostrini, R.; Carturan, G. *Inorg. Chim. Acta* **1988**, *142*, 187–189.

[41] The oxidative glycol cleavage reaction observed here is analogous in terms of the products formed to those commonly carried out with periodate and lead tetraacetate: Perlin, A. S. In *The Carbohydrates: Chemistry and Biochemistry*, 2nd ed.; Pigman, W. W., Horton, D., Eds.; Academic Press: New York, 1980; Vol. IB, pp 1167–1215.

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[43] Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969–2974.

[44] The primary Pt–P product formed under these conditions is $(dppe)_2Pt$ (**4**), apparently resulting from disproportionation of the $(dppe)Pt^0$ intermediate to give **4** and what appears to be colloidal platinum.

Vinylidene Complexes by M=C/N=C Metathesis from Benzylidene Complexes and Ketenimines

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Summary: Pentacarbonylbenzylidenetungsten adds triphenylketenimine to produce, after rearrangement, the imine adduct of pentacarbonyl(diphenylvinylidene)tungsten, which on thermolysis gives either an azetidinylidene complex or/and pentacarbonyl(diphenylvinylidene)tungsten.

Electrophilic transition-metal carbene complexes react with N=C double-bond systems (imines, carbodiimides, diaza dienes) in different ways. On photolysis of $(CO)_5M$-[C(R)R′] in the presence of imines β-lactams are formed.[1,2] Hegedus et al. proposed that the reaction is initiated by a photoinduced CO/carbene ligand coupling. The resulting ketene complex then reacts with imines to give the β-lactams. In contrast, the thermal reaction of alkoxy-

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[1] (a) McGuire, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538. (b) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833. (c) Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1109 and literature cited therein.

[2] Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.

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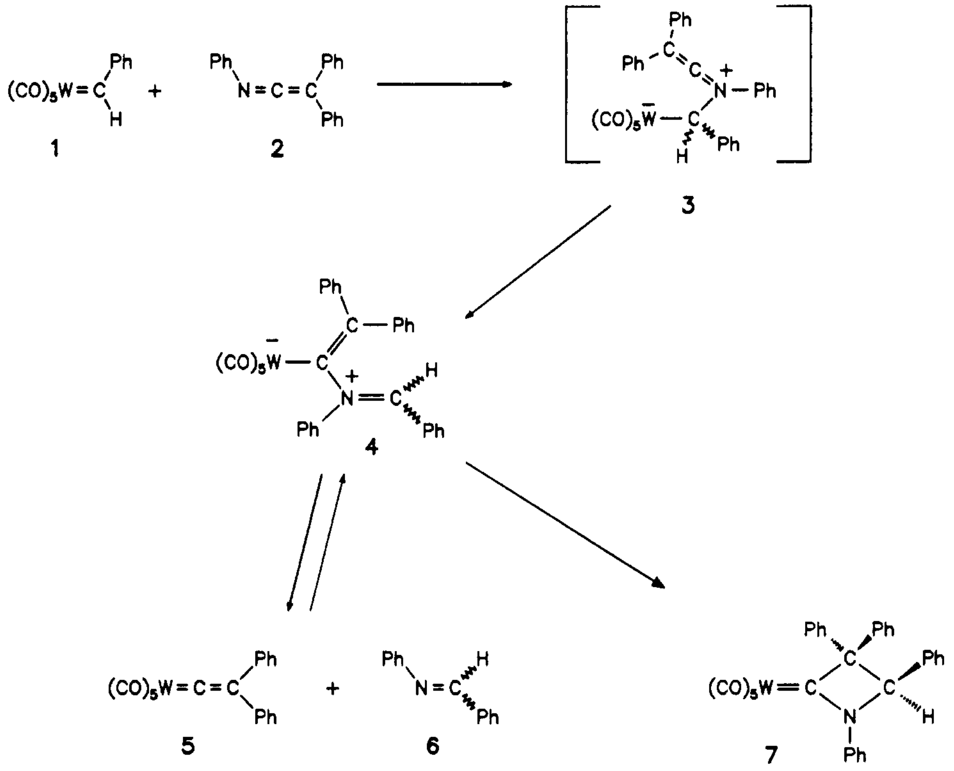
Scheme I



carbene complexes with imines leads to aminocarbene[2] and (alkylideneamino)carbene complexes,[3] respectively. Non-heteroatom-stabilized carbene complexes either add imines to the carbene carbon to give ylide complexes[4,5] or produce imino complexes and metathesis products.[4,5] The reactions of $(CO)_5M[C(R)R']$ with carbodiimides also lead to different products: (1) imines and isocyanide complexes (R = Ph, R′ = OMe),[6] (2) cyclic aminocarbene complexes (M = Cr, R = OH, R′ = Me),[7] (3) carbene anhydride complexes (M = Cr, R = OH, R′ = aryl),[8,9] and (4) carbene–carbyne complexes (M = W, R = OH, R′ = aryl, Me).[9,10] We now report the first formation of a vinylidene complex in the reaction of $(CO)_5W[C(Ph)H]$ (**1**)[11] with triphenylketenimine.

Even at −70 °C, the benzylidene complex **1** reacts quickly with an equimolar amount of triphenylketenimine (**2**) in dichloromethane. The dark red solution turns light red, and a red precipitate forms. Addition of pentane, followed by filtration and washing with pentane, gives the red complex **4** in ca. 80% yield. The IR data[12] and the poor solubility in nonpolar solvents are consistent with a zwitterionic pseudooctahedral pentacarbonyl structure. The ^{1}H NMR spectrum shows a singlet at δ 8.05 in addition to the phenyl resonances, in agreement with structure **4** (Scheme I) rather than with **3**. The structural assignment as an imine adduct of pentacarbonyl(diphenylvinylidene)tungsten (**5**) is further supported by the ^{13}C NMR spectrum. It shows three resonances in the olefinic region: δ 169.6, 165.2 (J_{WC} = 94.6 Hz), and 154.7. In the gated decoupling spectrum only the signal at δ 154.7 splits into a doublet (J_{CH} = 174.0 Hz). Therefore, the carbon bonded to tungsten does not carry a hydrogen atom. Thus, alternative structures such as **3** (diphenylketenimine adduct of **1**) or a metallaazacyclobutane (related to the chromadiazacyclobutane formed from $(CO)_5Cr[C(OMe)Me]$ and *cis*-azobenzene)[13] can be excluded.

The reaction of **1** with **2** is very likely initiated by a nucleophilic attack of **2** at the carbene carbon of **1** followed by rearrangement of **3** to **4**. There is extensive precedent for this type of "insertion" into a metal–carbene bond in the reactions of **1** with ethoxyacetylene,[11a] (diethylamino)propyne,[14] and diethylcyanamide[15] and of $(CO)_5W[C(OMe)Me]$ with, e.g., azobenzene.[16] The mode of formation of **4** is unknown. Several different pathways are conceivable, a mechanism involving a metallacyclic transition state being the most likely one. The rearrangement of **3** to **4** is rapid. Attempts to detect the proposed intermediate **3** by monitoring the conversion of **1** with **2** to **4** by ^{1}H NMR spectroscopy were unsuccessful. Even immediately after equimolar amounts of **1** and **2** are mixed in dichloromethane at −70 °C, no signals are present in the

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(3) (a) Knauss, L.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 3744. (b) Knauss, L.; Fischer, E. O. *J. Organomet. Chem.* **1971**, *31*, C68.

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(12) **4**: ν_{CO} (CH_2Cl_2, −35 °C) 2056, 1964, 1914, 1883 cm^{-1}; ^{1}H NMR (CD_2Cl_2, −70 °C) δ 6.7–7.8 (m, 18 H), 8.05 (s, 1 H), 8.34 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR (CD_2Cl_2, −55 °C) δ 154.7 (J_{CH} = 174.0 Hz), 165.2 (J_{WC} = 94.6 Hz), 169.6, 198.9 (J_{WC} = 127.1 Hz, cis CO), 201.8 (J_{WC} = 131.0 Hz, trans CO), and 16 signals between 119.1 and 146.4 (Ph); MS (EI) M$^+$ *m/e* 683 (^{184}W). Anal. Calcd for $C_{32}H_{21}NO_5W$: C, 56.24; H, 3.10; N, 2.05. Found: C, 56.76; H, 3.30; N, 2.20.

(13) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194.

(14) Fischer, H.; Schmid, J. *J. Mol. Catal.* **1988**, *46*, 277.

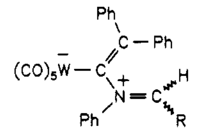
(15) Fischer, H.; Hofmann, J. Unpublished results.

(16) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700.

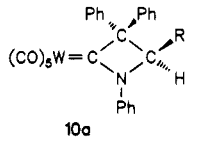
spectrum except those due to **4**. The greater stability of **4** compared to that of **3** is easily explained by the better delocalization of the positive charge at nitrogen in **4**.

In CH_2Cl_2 at room temperature **4** reacts within several minutes to produce a mixture of the green diphenylvinylidene complex **5**,[17] phenylbenzylideneamine (**6**), and the yellow azetidinylidene complex **7**.[18] The formation of **5** and **6** from **4** is reversible, as can be demonstrated by ^1H NMR and visible spectroscopy. When compound **4** is warmed in CD_2Cl_2 from −70 °C to ambient temperature, the red color of the solution changes to green due to the formation of **5**. Simultaneously, the $C(C_6H_5)H$ singlet of **4** at δ 8.05 disappears and a new singlet at δ 8.38 ($C(C_6H_5)H$ of **6**) appears. Cooling the solution to −70 °C again restores the red color of **4** and the singlet at δ 8.05. When solutions of **4** (or of **5** and **6**) are kept at ambient temperature for *prolonged* time, the acetidinylidene complex **7** is the exclusive product and is isolated after column chromatography in more than 80% yield. However, protonation of **6** by 1 equiv of $HBF_4{\cdot}Et_2O$ or addition of $BF_3{\cdot}Et_2O$ to solutions of **4** (before warmup) suppresses the readdition of **6** to **5** (to produce **4**). Then **5** is obtained from **4** after chromatographic workup of the reaction mixture in yields up to 90%. Thus, the main product can be predetermined by the choice of reaction conditions.

Complex **7** very likely is formed from **4** by an intramolecular cyclization and from **5** via fast readdition of **6** to give **4** followed by slow cyclization (Scheme I). The dissociation of **6** from **4** is reversible, whereas the formation of **7** is irreversible. Therefore, the ultimate reaction product is **7**, provided that the imine **6** is not removed from the reaction mixture by protonation or adduct formation with BF_3. This reaction scheme is supported by crossover experiments. When a solution of **4** in CD_2Cl_2 is warmed to ambient temperature for 20 min in the presence of 3 equiv of $(C_6H_5)N{=}C(C_6H_4OCH_3\text{-}p)H$ (**8a**) and then recooled to −70 °C, the ^1H NMR spectrum shows singlets for OCH_3 groups at δ 3.96 (**9a**) and 3.56 (**10a**) and a singlet at δ 8.44 ($(C_6H_5)CH$ of **6**) in addition to the singlets of **8a** at δ 3.83 (OCH_3) and 8.36 ($(C_6H_4OCH_3)CH$). In the course of several hours at 20 °C the intensity of the OCH_3 singlet at δ 3.96 (**9a**) decreases and that at δ 3.56 (**10a**) increases. From the reaction mixture the azetidinylidene complexes **7** and **10a**[19] are isolated (ratio ca. 1:2). Analogously, addition of **8a** to solutions of the pure diphenylvinylidene complex **5** affords adduct **9a**,[20] which converts to **10a** within hours at room temperature.



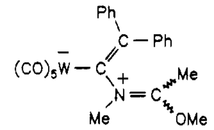
9a



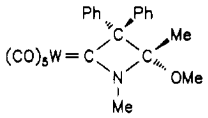
10a

R = $C_6H_4OCH_3$

Results similar to those with the system **4**/**8a** are obtained on thermolysis of **4** in the presence of $H_3CN{=}C(OCH_3)CH_3$ (**8b**), which affords a mixture of **6**, **7**, **9b**,[21] and **10b**.[22]



9b



10b

These findings are consistent with the proposed reaction scheme, but they do not completely rule out direct antarafacial addition of the imines **6** and **8a,b** to the C=C bond of **5** as an alternative (or additional) mechanism. The formation of azetidinylidene complexes (percursors of β-lactams) from cationic iron vinylidene complexes and imines is well-known.[23] A stepwise path was proposed by Barrett et al. and confirmed by the isolation of the intermediate $\{Cp[(MeO)_3P](CO)FeC[{=}CMe_2][N(Me){=}C(Ph)H]\}^+CF_3SO_3^-$. Similarly, the β-lactam formation in the reaction of diphenylketene with benzalaniline was suggested to proceed via a zwitterion.[24] A vinylidene complex, $(CO)_5Cr{=}C{=}CH_2$, was also proposed as an intermediate in the reaction of $(CO)_5Cr{=}C(OH)Me$ with dicyclohexylcarbodiimide.[25]

The formation of **5** and **6** from **1** and **2** constitutes a novel route for the synthesis of vinylidene complexes. This method, which corresponds to a M=C/N=C metathesis, should be useful especially in the preparation of vinylidene complexes not accessible by other routes (as e.g. **5**).

Acknowledgment. We thank the Stiftung Volkswagenwerk and the Fonds der Chemischen Industrie for financial support.

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(17) **5**: ν_{CO} (pentane) 2096 m, 2006 s, 1991 s, 1977 vs cm^{-1}; ^1H NMR ($CDCl_3$, −5 °C) δ 7.41 (m, 2 H), 7.28 (m, 3 H); ^{13}C NMR ($CDCl_3$, −23 °C) δ 127.2, 128.3, 128.6, 129.0 (Ph), 131.9 (J_{WC} = 20.8 Hz, β-C), 192.6 (J_{WC} = 126.0 Hz, cis CO), 208.9 (J_{WC} = 96.8 Hz, trans CO), 375.1 (J_{WC} = 118.2 Hz, α-C); MS (EI) M^+ *m/e* 502 (^{184}W). Anal. Calcd for $C_{19}H_{10}O_5W$: C, 45.45; H, 2.01. Found: C, 45.52; H, 2.03.

(18) **7**: ν_{CO} (pentane) 2066 m, 1980 w, 1942 s, 1936 vs cm^{-1}; ^{13}C NMR ($CDCl_3$, −10 °C) δ 73.0, 83.0, 16 signals between 124.4 and 140.1 (Ph), 197.1 (J_{WC} = 127.6 Hz, cis CO), 201.9 (trans CO), 277.3 (carbene C). Anal. Calcd for $C_{23}H_{21}NO_5W{\cdot}{}^1/_2C_5H_{12}$: C, 57.60; H, 3.78; N, 1.94. Found: C, 57.42; H, 3.84; N, 2.00.

(19) **10a**: ν_{CO} (hexane) 2066 m, 1980 m, 1942 s, 1936 vs cm^{-1}; ^1H NMR (CD_2Cl_2, −70 °C) δ 3.56 (s, 3 H), 6.5–6.8 (m, 4 H), 7.1–7.7 (m, 16 H).

(20) **9a**: ^1H NMR (CD_2Cl_2, −70 °C) δ 3.96 (s, OCH_3), 6.9–7.6 (m, C_6H_4 and C_6H_5), 7.91 (N=C*H*).

(21) **9b**: ^1H NMR (CD_2Cl_2, −70 °C) δ 2.09 (CH_3), 3.16 (NCH_3), 4.12 (OCH_3), 6.8–7.7 (m, Ph).

(22) **10b**: ν_{CO} (pentane) 2065 m, 1980 w, 1932 m sh, 1935 vs cm^{-1}; ^1H NMR (CD_2Cl_2, 20°C) δ 2.49 (CH_3), 3.34 (NCH_3), 3.83 (OCH_3), 6.8–7.6 (m, Ph).

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