

Mechanism of the Formation of Platina- β -diketones: A DFT Study[†]

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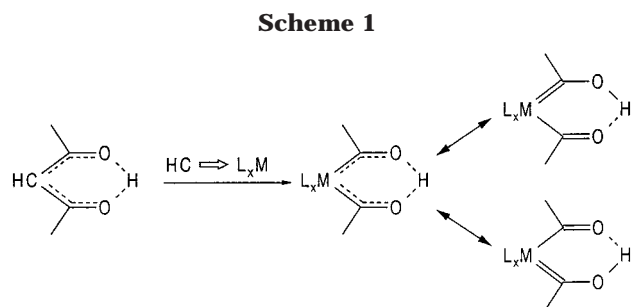
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Based on experimental findings that formation of dinuclear platina- β -diketones [Pt₂(μ -Cl₂{(COR)₂H}₂}] from reactions of hexachloroplatinic acid with silylated alkynes R'C≡CSiMe₃ (R = CH₂R') proceeds most likely via terminal alkyne complexes of Zeise's salt type [PtCl₃(η^2 -R'C≡CH)]⁻, DFT calculations using the hybrid functional B3LYP of reaction mechanism were performed. Reaction of propyne complex [PtCl₃(η^2 -MeC≡CH)]⁻, **10**, with MeC≡CH and OH⁻/H₂O affording mononuclear platina- β -diketonate anion [PtCl₂{(COEt)₂H}]⁻, **11**, was used as a model. Formation of complex **11** from complex **10** proved to be strongly exothermic ($\Delta E = -176.8$ kcal/mol). Four reaction types were taken into consideration: (a) equilibration (tautomerization) between alkyne and vinylidene complexes, (b) substitution of a chloro ligand by an alkyne, (c) addition of water to a vinylidene ligand affording a hydroxycarbene ligand, and (d) deprotonation of a hydroxycarbene ligand affording an acyl ligand. Results show that the reaction proceeds as follows: Alkyne complex [PtCl₃(η^2 -MeC≡CH)]⁻, **10**, equilibrates to vinylidene complex [PtCl₃(C=CHMe)]⁻, **12** ($\Delta E = 0.9$ kcal/mol), which adds water, yielding hydroxycarbene complex [PtCl₃{C(OH)Et}]⁻, **17** ($\Delta E = -45.6$ kcal/mol). Complex **17** is deprotonated by OH⁻, affording doubly negatively charged acyl complex [PtCl₃{C(O)Et}]²⁻, **19** ($\Delta E = -28.8$ kcal/mol). Complex **19** reacts with propyne, giving acyl-propyne complex [PtCl₂{C(O)Et}(η^2 -MeC≡CH)]⁻, **20** ($\Delta E = -53.0$ kcal/mol). Equilibration to the corresponding acyl-vinylidene complex [PtCl₂{C(O)Et}(C=CHMe)]⁻, **21** ($\Delta E = 2.0$ kcal/mol), and addition of water to the vinylidene ligand affords mononuclear platina- β -diketonate anion [PtCl₂{(COEt)₂H}]⁻, **11** ($\Delta E = -52.3$ kcal/mol). Apart from alkyne-vinylidene equilibration reactions being very weakly endothermic ($\Delta E < 2$ kcal/mol), all reactions steps are strongly exothermic ($\Delta E < -28$ kcal/mol). Other pathways for formation of complex **11** from **10** which had been considered proved to contain one strongly endothermic step ($\Delta E > 39$ kcal/mol). There are no indications for a kinetic reaction control. Thus, in the formation of platina- β -diketonate anion **11** deprotonation of the hydroxycarbene ligand affording an acyl ligand proceeds as the earliest possible stage of reaction. Dimerization of complex **11** with cleavage of two chloride anions affords dinuclear platina- β -diketone complex [Pt₂(μ -Cl)₂{(COEt)₂H}₂], **22**, in an endothermic reaction ($\Delta E = 57.4$ kcal/mol). But the energy demand for dimerization will be overcompensated by the strongly exothermic formation of complex **11**, and the resulting value for the formation of **22** from **10** can be estimated to be about -296 kcal/mol. All intermediate complexes were calculated without symmetry restrictions. Their structures will be discussed.

1. Introduction

Metalla- β -diketones are formally related to enol forms of organic β -diketones where the central CH methine unit has been replaced by a metal fragment L_xM (Scheme 1). As the canonical structures given in Scheme 1 exhibit, metalla- β -diketones can be regarded as complexes with cis standing hydroxycarbene and acyl ligands that are intramolecularly stabilized by hydrogen bonding. Metalla- β -diketones of the type [M{(COR)₂H}-L_x], **1** (M = Mn, Re, Fe, ...; L = CO, Cp, ...), were intensively investigated by Lukehart.¹ Their way of

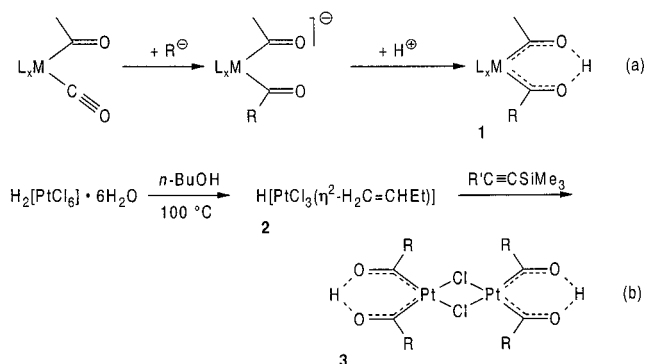


formation via alkylation of acyl-carbonyl-metal complexes and protonation of the anionic diacyl complex (Scheme 2a) makes clear that all these complexes are electronically saturated (18 valence electrons) having a kinetically inert ligand sphere. Another type of met-

[†] Dedicated to Professor Rudolf Taube on the occasion of his 70th birthday.

(1) (a) Lukehart, C. M. *Acc. Chem. Res.* **1981**, *14*, 109. (b) Lukehart, C. M. *Adv. Organomet. Chem.* **1986**, *25*, 45.

Scheme 2



b) R = Me, Et, *n*-Pent, *n*-Hex, (CH₂)₄Ph; R' = R - CH₂.

alla- β -diketones is formed when hexachloroplatinic acid is reduced by *n*-butanol at about 100 °C, yielding Zeise's acid with butene as ligand **2**, which reacts with alkylnitrimethylsilanes under formation of dinuclear platina- β -diketones **3** (Scheme 2b).² Contrary to Lukehart's metalla- β -diketones, they are electronically unsaturated complexes (16 valence electrons) with kinetically labile ligand spheres.

In this paper we report quantum chemical calculations at the DFT level of theory using the hybrid functional B3LYP on the mechanism of formation of dinuclear platina- β -diketones **3**. Possible intermediates are alkyne, vinylidene, hydroxycarbene, and acyl platinum complexes. To build up *one* metalla- β -diketone unit consisting formally of one hydroxycarbene *and* one acyl moiety (cf. Scheme 1), reaction from alkyne complex to hydroxycarbene and acyl moiety, respectively, has to proceed twice. Investigations are directed to find out the correct reaction sequence.

2. Computational Details

All DFT calculations were carried out by the Gaussian98³ program package using the hybrid functional B3LYP.⁴ For the main group atoms the basis set 6-31G*⁵ was employed. The valence shell of platinum has been approximated by a split valence basis set too; for its core orbitals an effective core potential in combination with consideration of relativistic effects has been used.⁶ All systems have been fully optimized

(2) (a) Steinborn, D.; Gerisch, M.; Merzweiler, K.; Schenzel, K.; Pelz, K.; Bögel, H.; Magull, J. *Organometallics* **1996**, *15*, 2454. (b) Steinborn, D.; Gerisch, M.; Hoffmann, T.; Bruhn, C.; Israel, G.; Müller, F. W. *J. Organomet. Chem.* **2000**, *598*, 286.

(3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.3*; Gaussian Inc.: Pittsburgh, PA, 1998.

(4) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(5) Levine, I. N. *Quantum Chemistry*; Prentice Hall International: London, 1991; p 463.

(6) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of the normal vibrations. Zero-point energies calculated by means of the B3LYP functional were scaled by a factor of 0.91.⁷ Because of the high number of non-hydrogen atoms in the dimeric platina- β -diketone **22**, no zero-point corrections could be carried out. Atomic charges and bond orders were obtained by the natural bond orbital (NBO) analysis of Reed et al.⁸ as implemented in Gaussian98.

3. Results and Discussion

3.1. Experimental Background. The only intermediate in the formation of platina- β -diketones **3** identified so far is complex **2** (Scheme 2b), which could be isolated and characterized as a PPN salt (PPN⁺ = μ -nitrido-bis-(triphenylphosphorus) cation) from the reaction mixtures.⁹ Further experimental findings are that (i) the second reaction in Scheme 2b is strongly exothermic, (ii) the trimethylsilyl groups cleaved off form mainly Me₃Si-O-SiMe₃, and (iii) butene is a side product. A plausible mechanism for the formation of platina- β -diketones is shown in Scheme 3. It includes the formation of an alkyne complex **4** by ligand substitution reaction (Scheme 3, a). Cleavage of the \equiv C-Si bond results in formation of a platinum(II) complex **5** with a terminal alkyne ligand (b) that is in equilibrium with vinylidene complex **6** (c). Addition of water forms a hydroxycarbene complex **7a** (d), whose deprotonation results in formation of an acyl complex **7b** (e). Complexes **7a** and **7b** are the two building blocks for platina- β -diketones.

All reactions assumed here are experimentally verified in organometallic chemistry. Alkyne complexes of Zeise's salt type [K(18C6)][PtCl₃(η^2 -RC \equiv CR')] (18C6 = crown ether 18-crown-6) are known, among them those with terminal alkynes (see complex **5** in Scheme 3).¹⁰ The cleavage of alkynyl-silicon bonds (see reaction b in Scheme 3) is well known and commonly used in organic synthesis.¹¹ With cleavage of \equiv C-Si bonds the reaction of H₂PtCl₆·6H₂O with Me₃SiC \equiv CH in propan-2-ol proceeds, yielding the bis(isopropoxycarbene) complex [PtCl₂{C(O*i*Pr)Me₂}₂], **8**.¹² Cationic platinum(II) complexes *trans*-[PtR(PR')₂(R''OH)]PF₆ (R = H, Me, R' = alkyl, aryl, R'' = Me, Et) were found to react with Me₃SiC \equiv CH or Me₃SiC \equiv CMe, yielding cationic alkoxy-carbene complexes *trans*-[PtR(PR')₂{C(OR'')Me}]PF₆, **9a**, and *trans*-[PtR(PR')₂{C(OR'')Et}]PF₆, **9b**, respectively. With Me₃SiC \equiv CSiMe₃ the same product as with Me₃SiC \equiv CH was obtained.¹³ Likely, both reactions proceed via η^2 -Me₃SiC \equiv CR (R = H, Me, SiMe₃) com-

(7) Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128, and references therein.

(8) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

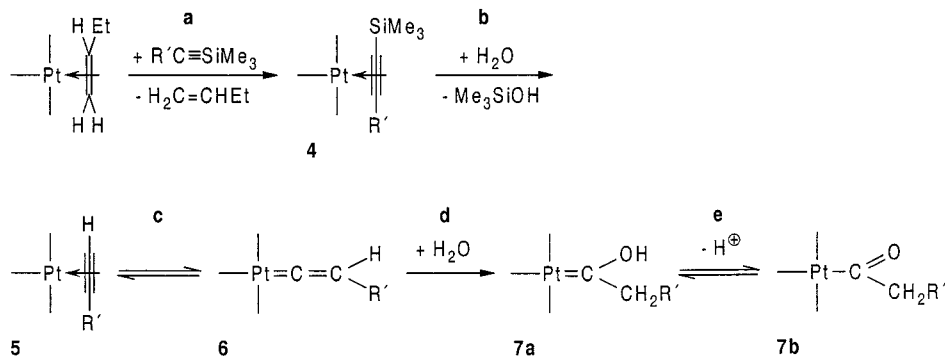
(9) Steinborn, D.; Nünthel, R.; Sieler, J.; Kempe, R. *Chem. Ber.* **1993**, *126*, 2393.

(10) (a) Steinborn, D.; Tschöerner, M.; Zweidorf, A. v.; Sieler, J.; Bögel, H. *Inorg. Chim. Acta* **1995**, *234*, 47. (b) Gerisch, M.; Heinemann, F. W.; Bögel, H.; Steinborn, D. *J. Organomet. Chem.* **1997**, *548*, 247.

(11) Furber, M. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: New York, 1995; Vol. 1, p 997.

(12) Struchkov, Y. T.; Aleksandrov, G. G.; Pukhnarevich, V. B.; Sushchinskaya, S. P.; Voronkov, M. G. *J. Organomet. Chem.* **1979**, *172*, 269.

(13) Clark, H. C.; Jain, V. K.; Rao, G. S. *J. Organomet. Chem.* **1983**, *259*, 275.

Scheme 3^a

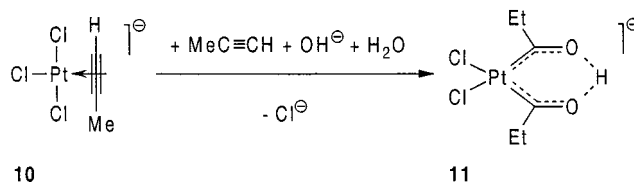
^a Charges are omitted.

plexes as intermediates. Formation of complexes **8** and **9** could include the same reaction steps (a–d) as described in Scheme 3. But instead of addition of water yielding hydroxycarbene moieties whose deprotonation affords platina- β -diketones, ROH is added in step **d**, providing stable alkoxycarbene complexes. Furthermore, cleavage of =C–Si bonds in 2-silylvynylidene complexes $L_xM=C=CH(SiMe_3)$ ($M = Rh^I, Fe^0, Ru^{II}, Re^I$) results under mild reaction conditions (H_2O, H^+ , chromatography on Al_2O_3 or SiO_2) in formation of $L_xM=C=CH_2$.¹⁴

Isomerization (tautomerization) of alk-1-yne to vinylidenes on metal centers (see reaction **c** in Scheme 3) is a basic reaction in alkyne chemistry.¹⁵ Addition of water or OH^- to vinylidene complexes affording hydroxycarbene complexes (see reaction **d** in Scheme 3) is experimentally verified.^{14d,16} Proton exchange between hydroxycarbene and acyl complexes (see reaction **e** in Scheme 3) is a common reaction.^{14c,16b,17} Furthermore, protonation of acyl ligands yielding hydroxycarbene moieties is a reaction step of the classical Fischer synthesis of carbene complexes¹⁸ and the last step of Lukehart's metalla- β -diketone synthesis.¹

3.2. Reaction Pathways. As a model reaction for DFT studies we chose the reaction of the trichloro(propyne)platinate(II) anion **10** with propyne in the presence of hydroxide ions to provide the anionic mononuclear platina- β -diketone **11** (Scheme 4). Calculations

Scheme 4



were performed in the gas phase, and solvation effects were not considered. The overall reaction proved to be strongly exothermic ($\Delta E = -176.8$ kcal/mol). Taking into account the principal mechanism described above, there are three reasonable pathways for the formation of **11** starting with **10** (Figure 1):

Route A: Ligand Substitution (Cl^- vs propyne) Dominates over Hydroxycarbene Formation (Pathway $10 \rightarrow 12 \rightarrow 13 \rightarrow 14 \rightarrow 15 \rightarrow 16 \rightarrow 11$). Alkyne complex **10** is in equilibrium with vinylidene complex **12**, which undergoes a ligand substitution reaction (Cl^- vs propyne) yielding alkyne–vinylidene complex **13** and corresponding bis(vinylidene) complex **14** as key intermediates. Successive addition of water and deprotonation results in formation of platina- β -diketone **11**.

Route B: Hydroxycarbene Formation Dominates over Ligand Substitution (Cl^- vs propyne) (Pathway $10 \rightarrow 12 \rightarrow 17 \rightarrow 18 \rightarrow 15 \rightarrow 16 \rightarrow 11$). Alkyne complex **10** is in equilibrium with vinylidene complex **12**, which adds water, yielding hydroxycarbene complex **17**. Ligand substitution (Cl^- vs propyne) and alkyne–vinylidene tautomerization results via complex **18** in formation of the hydroxycarbene–vinylidene complex **15**. Complex **15** reacts as described in route A, forming platina- β -diketone **11**.

Route C: Acyl Complex Formation Dominates over Ligand Substitution (Cl^- vs propyne) (Pathway $10 \rightarrow 12 \rightarrow 17 \rightarrow 19 \rightarrow 20 \rightarrow 21 \rightarrow 11$). Hydroxycarbene complex **17** formed as described in route B undergoes a deprotonation, yielding the doubly negatively charged acyl complex **19**. Ligand substitution reaction (Cl^- vs propyne) and alkyne–vinylidene tautomerization results via intermediate complex **20** in formation acyl–vinylidene complex **21**, which reacts with water, directly yielding platina- β -diketone complex **11**.

Geometries of all these intermediates were fully optimized without symmetry restrictions. The three pathways discussed here include four reaction types: (a) equilibration (tautomerization) between alkyne and vinylidene complexes, (b) substitution of a chloro ligand by an alkyne, (c) addition of water to a vinylidene ligand

(14) (a) Rappert, T.; Nürnberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359. (b) Gauss, C.; Veghini, D.; Berke, H. *Chem. Ber./Recl.* **1997**, *130*, 183. (c) Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R. *Organometallics* **1996**, *15*, 3804. (d) Katayama, H.; Ozawa, F. *Organometallics* **1998**, *17*, 5190.

(15) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(16) (a) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169. (b) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585. (c) Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1978**, *155*, C8.

(17) (a) Grötsch, G.; Malisch, W. *J. Organomet. Chem.* **1983**, *246*, C42. (b) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1069. (c) Lilga, M. A.; Ibers, J. A. *Organometallics* **1985**, *4*, 590. (d) Grundy, K. R.; Jenkins, J. *J. Organomet. Chem.* **1984**, *265*, 77. (e) Barratt, D. S.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1986**, *306*, C41. (f) Barratt, D. S.; Glidewell, C.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1079. (g) Gauntlett, J. T.; Mann, B. E.; Winter, M. J.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **1991**, 1427. (h) Macdougall, J. K.; Simpson, M. C.; Cole-Hamilton, D. J. *Polyhedron* **1993**, *12*, 2877. (i) Bernasconi, C. F.; Flores, F. X.; Sun, W. *J. Am. Chem. Soc.* **1995**, *117*, 4875. (j) Casey, C. P.; Czerwinski, C. J.; Fusie, K. A.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 3971.

(18) (a) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651. (b) Fischer, H. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983; p 1.

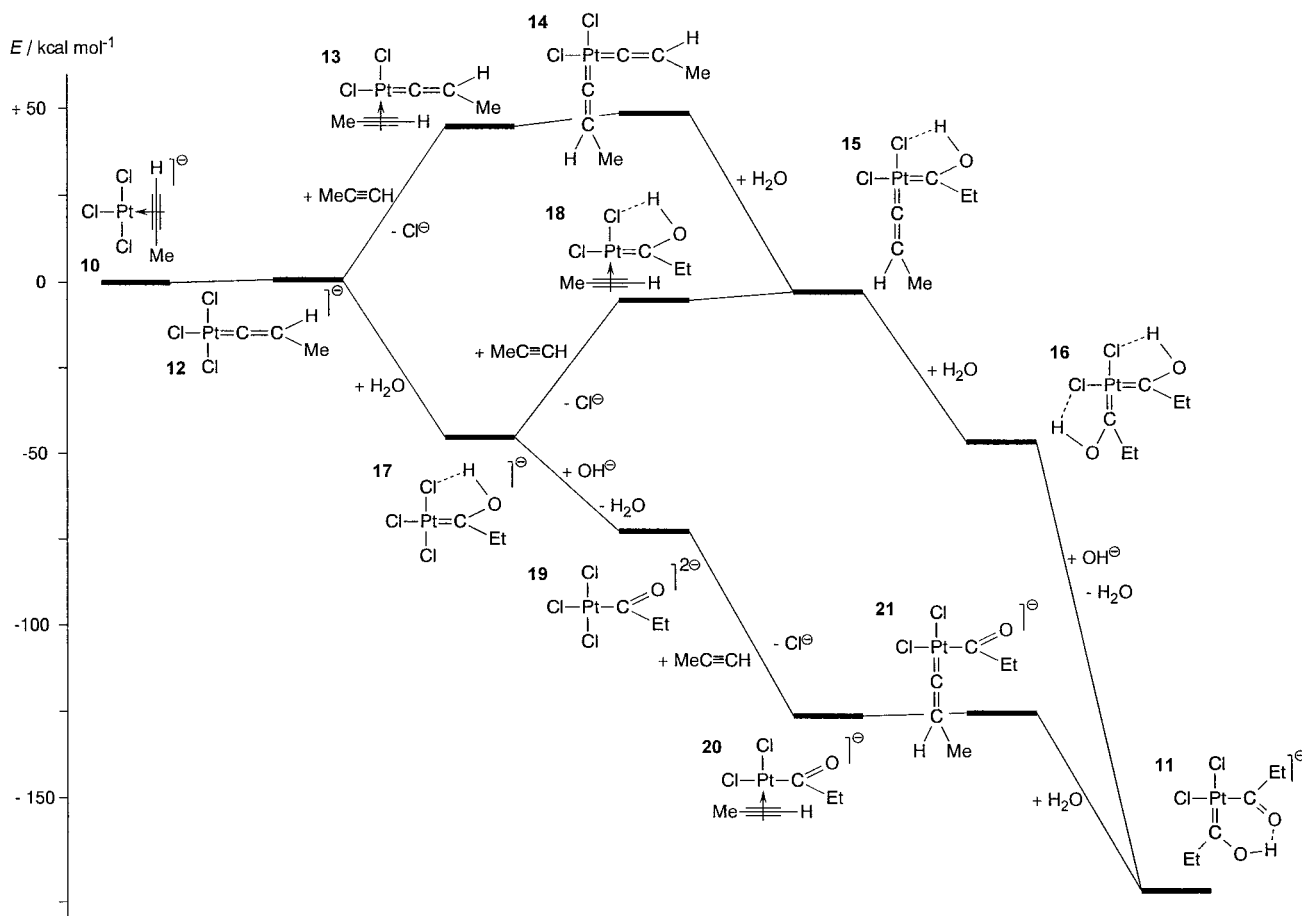


Figure 1. Reaction pathways for the formation of platina- β -diketone complex **11** from π -propyne complex **10**. Overall reaction see Scheme 4. Route A: **10** \rightarrow **12** \rightarrow **13** \rightarrow **14** \rightarrow **15** \rightarrow **16** \rightarrow **11**. Route B: **10** \rightarrow **12** \rightarrow **17** \rightarrow **18** \rightarrow **15** \rightarrow **16** \rightarrow **11**. Route C: **10** \rightarrow **12** \rightarrow **17** \rightarrow **19** \rightarrow **20** \rightarrow **21** \rightarrow **11**.

affording a hydroxycarbene ligand, and (d/d') deprotonation of a hydroxycarbene ligand affording an acyl ligand using OH^- (d) or with cleavage of HCl (d'). The energies of all these reactions are summarized in Table 1.

3.3. Equilibration between Alkyne and Vinylidene Complexes. Selected structural parameters of π -propyne and prop-1-enylidene complexes calculated in this work are given in Tables 2 and 3. As examples, structures of the π -propyne complex **10** and of the corresponding prop-1-enylidene complex **12** are shown in Figure 2. All π -propyne complexes (**10**, **13**, **18**, **20**) exhibit the expected structures. The propyne ligand is approximately perpendicular to the complex plane (83.2 – 89.6°). Due to coordination, $\text{C}\equiv\text{C}$ triple bonds are slightly lengthened (1.238 – 1.249 Å) compared with the noncoordinated propyne (1.207 Å).¹⁹ The substituents at the acetylenic carbon atoms (H/Me) are bent away from the $\text{C}\equiv\text{C}$ line, as the angles $\text{C}\equiv\text{C}-\text{C}$ (163.7 – 169.0°) and $\text{C}\equiv\text{C}-\text{H}$ (158.1 – 161.6°) exhibit. Similar values ($\text{C}\equiv\text{C}$ $1.22(2)$ – $1.25(2)$ Å, $\text{C}\equiv\text{C}-\text{C}$ $159(2)$ – $164.8(9)^\circ$) were found in alkyne complexes of Zeise's salt type $[\text{K}(18\text{C}6)][\text{PtCl}_3(\eta^2\text{-RC}\equiv\text{CR}')] (R/R' = \text{Me/Me; Et/Et; Ph/H; 18C6} = \text{crown ether 18-crown-6})$.¹⁰ There is a good linear correlation between $\text{C}\equiv\text{C}$ bond lengths and bond

orders $\text{BO}_{\text{C}=\text{C}}$ ($r = 0.99$, 4 data points). These values show (Table 2) that π back-donation in anionic complexes **10** and **20** is slightly larger than in neutral complexes **13** and **18**.

Prop-1-enylidene complexes **12**, **13**, **14**, **15**, and **21** have nearly linear $\text{Pt}=\text{C}=\text{C}$ groups (175.8 – 179.5°). Vinylidene planes are approximately perpendicular to complex planes (83.4 – 89.9°). Bond orders $\text{BO}_{\text{C}=\text{C}}$ and $\text{C}=\text{C}$ bond lengths are well correlated ($r = 1.00$, 5 data points) (Figure 3). An analogous dependence was found for bond orders $\text{BO}_{\text{Pt}=\text{C}}$ and $\text{Pt}=\text{C}$ bond lengths ($r = 0.94$, $n = 5$ data points). Compared with the noncoordinated prop-1-enylidene (calculated at the same level of theory), $\text{C}=\text{C}$ bonds are lengthened in anionic complexes **12** and **21** (1.307 – 1.309 vs 1.304 Å) and shortened in neutral complexes **13**–**15** (1.296 – 1.299 vs 1.304 Å).

Vinylidene ligands have two π -acceptor orbitals, namely, in-plane p AO at the carbenic center (C_α) and the π^* orbital of $\text{C}=\text{C}$ bond.²⁰ NBO analysis exhibits that in all complexes occupation of $\text{p}_{\text{C}_\alpha}$ orbitals is fairly high and varies between 0.500 and 0.548. Occupation of $\pi^*_{\text{C}=\text{C}}$ orbitals is lower and markedly dependent on total charge of complexes: 0.117–0.124 for anionic complexes vs 0.091–0.105 for neutral complexes. Occupation of $\pi^*_{\text{C}=\text{C}}$ orbitals gives rise to lengthening of $\text{C}=\text{C}$ bonds (Figure 3). These findings exhibit that π back-donation in anionic complexes **12** and **21** is of

(19) Calculated at the same level of theory. The experimental value amounts to $1.2073(50)$ Å: Landolt-Börnstein. *Numerical Data and Functional Relationships in Science and Technology, New Series II/7*; Springer-Verlag: Berlin, 1976.

(20) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

Table 1. Calculated Reaction Energies for Reactions Shown in Figure 1

reaction type	n	reaction	ΔE in kcal/mol
a	1-	10 \rightarrow 12	0.9
	1-	20 \rightarrow 21	2.0
	0	13 \rightarrow 14	6.0
	0	18 \rightarrow 15	3.1
b	1-	12 \rightarrow 13	42.1
	1-	17 \rightarrow 18	39.3
	2-	19 \rightarrow 20	-53.0
c	1-	12 \rightarrow 17	-45.6
	1-	21 \rightarrow 11	-52.3
	0	14 \rightarrow 15	-51.3
	0	15 \rightarrow 16	-44.0
d	1-	17 \rightarrow 19	-28.8
	0	16 \rightarrow 11	-130.4
	0	18 \rightarrow 20 ^a	-121.1
	0	15 \rightarrow 21 ^a	-122.2
d'	1-	17 \rightarrow 19 ^a	7.9

^a Not shown in Figure 1.

Table 2. Selected Structural Parameters of π -Propyne Complexes [PtCl₂X(η^2 -MeC \equiv CH)]ⁿ (bond lengths in Å, angles in deg)

	10	13	18	20
X	Cl	C=CHMe	C(OH)Et	C(O)Et
n	1-	0	0	1-
Pt-C	2.124/2.156	2.292/2.204	2.154/2.221	2.127/2.161
C \equiv C/BO ^a	1.248/2.368	1.238/2.448	1.244/2.397	1.249/2.369
C \equiv C-C	163.7	169.0	166.3	164.8
C \equiv C-H	159.8	161.6	159.7	158.1
Pt-Cl _{trans}	2.361	2.337	2.377	2.385
Pt-Cl _{cis}	2.384/2.384	2.357	2.379	2.533
Cl-Pt-Cl	90.6/90.6	91.1	90.1	91.9
PtC \equiv C/PtCl ₂	89.6/89.6	83.2	84.9	88.1

^a Bond order (given in electron pairs).

more importance than in neutral complexes **13**, **14**, and **15**.

For the theoretical level employed here (B3LYP/6-31G*) noncomplexed prop-1-enylidene is 45.9 kcal/mol higher in energy than propyne. This value is in good agreement with those for acetylene/vinylidene system both from calculations and from experimental studies.²¹ Within this work, the mechanism of conversion of alkyne into vinylidene (least-motion 1,2-H shift vs C-H oxidative addition followed by 1,3-H shift)^{21c,d,22} was not investigated.

Conversion of π -propyne complexes into the corresponding prop-1-enylidene complexes (reaction type a; Table 1) is weakly endothermic in all cases (ΔE 0.9–6.0 kcal/mol). Pt(II) allows π back-donation to a small extent only. The total d electron density on Pt can be

regarded as a measure for back-donation to all ligands. Table 4 shows the calculated difference of the total d electron density between alkyne and corresponding vinylidene complexes. These values are positive for all cases, showing that the vinylidene ligands demand more π electron density than the alkyne ligands. Two factors seem to be important for energy relations: (i) Negatively charged complexes are more capable of back-donation than neutral ones. Thus, reactions **10/12** and **20/21** are less endothermic than reactions **18/15** and **13/14**. (ii) π -Acceptor co-ligands destabilize vinylidene binding more than propyne binding. Thus, reactions with C(OH)Et and C=CHMe co-ligands are more endothermic than those with Cl and C(O)Et co-ligands.

In bis(vinylidene) complex **14** both vinylidene ligands include the same angle with the complex plane (87.8°), resulting in a sharing of platinum π orbitals for π back-donation. This seems slightly to decrease stability, and accordingly, the reaction yielding complex **14** is the most endothermic one.

3.4. Ligand Substitution Reaction (Cl⁻ vs propyne). Formation of platina- β -diketone complex **11** according to Figure 1 affords substitution of a chloro

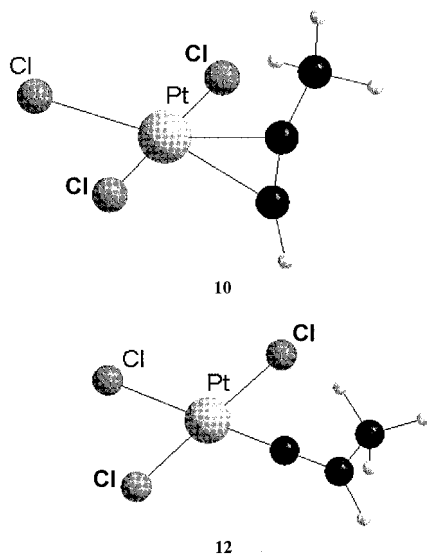
(21) (a) Chen, Y.; Jonas, D. M.; Hamilton, C. E.; Green, P. G.; Kinsey, J. L.; Field, R. W. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 329. (b) Gallo, M. M.; Hamilton, T. P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1990**, *112*, 8714. (c) Stegmann, R.; Frenking, G. *Organometallics* **1998**, *17*, 2089. (d) Pérez-Carreño, E.; Paoli, P.; Ienco, A.; Mealli, C. *Eur. J. Inorg. Chem.* **1999**, 1315.

(22) (a) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105. (b) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360.

Table 3. Selected Structural Parameters of Prop-1-enylidene Complexes [PtCl₂X(C=CHMe)]ⁿ (bond lengths in Å, angles in deg)

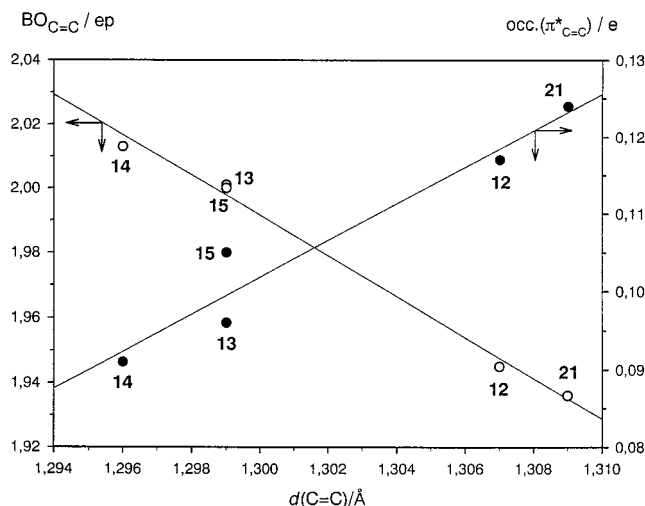
	12	13	14 ^a	15	21
X	Cl	MeC≡CH	C=CHMe	C(OH)Et	C(O)Et
n	1-	0	0	0	1-
Pt=C/BO ^b	1.832/1.194	1.866/1.023	1.883/0.956	1.858/0.989	1.837/1.196
C=C/BO ^b	1.307/1.945	1.299/2.001	1.296/2.013	1.299/2.000	1.309/1.936
Pt=C=C	179.5	179.0	178.8	175.8	178.3
C=C-C	124.4	125.4	125.5	125.0	124.2
Pt-Cl _{trans}	2.380	2.357	2.356	2.401	2.400
Pt-Cl _{cis}	2.387/2.387	2.337	2.356	2.373	2.511
Cl-Pt-Cl	90.7/90.7	91.1	91.1	90.7	91.9
C _{Me} -C=C-H ^c	180.0	178.0	177.7	177.2	177.7
C _{Me} -C-H/PtCl ₂	89.9	89.1	87.8	83.4	88.0
occ.(p _{Cα})	0.533	0.525	0.546	0.500	0.548
occ.(π^* _{C=C})	0.117	0.096	0.091	0.105	0.124

^a Complex exhibits C₂ symmetry. ^b Bond order (given in electron pairs). ^c Dihedral angle C_{Me}-C _{β} =C _{α} -H showing the planarity of the vinylidene ligand.

**Figure 2.** Calculated structures of π -propyne complex [PtCl₃(η^2 -MeC≡CH)]⁻, **10**, and corresponding prop-1-enylidene complex [PtCl₃(C=CHMe)]⁻, **12**.

ligand by propyne (reaction type b). Depending on the pathway, the starting complex is **12**, **17**, or **19** (Table 5). The reactions are strongly endothermic for the singly negatively charged complexes **12** and **17**. Obviously, this is due to loss of charge delocalization. Ligand substitution reaction starting from the doubly negatively charged complex **19** is strongly exothermic because there is a decrease in electrostatic repulsion due to charge separation. The small difference in reaction energy between the first two reactions **12/13** and **17/18** (42.1 vs 39.3 kcal/mol) may be due to the higher charge on platinum in the starting complex **12** compared with that in **17** ($\Delta q(\text{Pt}) = 0.092$, Table 5) and due to the stronger binding of propyne in the product complex **13** than that in **18** (cf. C≡C bond lengths and bond orders, Table 2). Both these effects are related with greater π -acceptor strength of vinylidene co-ligands in **12/13** compared with that of hydroxycarbene co-ligands in **17/18**.

3.5. Hydroxycarbene Complex Formation. Selected structural parameters of hydroxycarbene complexes calculated in this work are given in Table 6. As an example the structure of hydroxycarbene complex **17** is shown in Figure 4. A characteristic feature of all these complexes (**15–18**) is hydrogen bonding between

**Figure 3.** Dependence of C=C bond lengths (in Å) in prop-1-enylidene complexes on bond orders of C=C bonds (in electron pairs, ep) (open circles) and on occupation of π^* orbitals of C=C bonds (in electrons, e) (solid circles). Regression lines ($d(\text{C}=\text{C})$ vs $\text{BO}(\text{C}=\text{C})$, $r = 1.00$; $d(\text{C}=\text{C})$ vs $\text{occ.}(\pi^*_{\text{C}=\text{C}})$, $r = 0.97$) are shown.**Table 4. Electronic and Energetic Balance for the Interconversion between π -Propyne and Prop-1-enylidene Complexes**

reaction	co-ligand	total charge	$\Delta(\text{occ.})^a$	ΔE in kcal/mol
10 → 12	Cl	1-	1.786	0.9
20 → 21	C(O)Et	1-	2.325	2.0
18 → 15	C(OH)Et	0	1.816	3.1
13 → 14	C=CHMe	0	3.583	6.0

^a Difference in the occupation of the lone pair orbitals on platinum between π -propyne and prop-1-enylidene complex given in electrons.

Table 5. Electronic and Energetic Balance for the Ligand Substitution Reactions (Cl⁻ vs Propyne)

reaction	co-ligand	total charge ^a	$q(\text{Pt})^b$	ΔE in kcal/mol
12 → 13	C=CHMe	1-	0.626	42.1
17 → 18	C(OH)Et	1-	0.534	39.3
19 → 20	C(O)Et	2-	0.400	-53.0

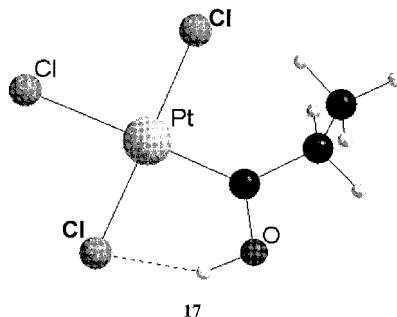
^a Given for the starting complex. ^b Given in electrons.

the hydroxyl group of the hydroxycarbene ligand and the cis standing chloro ligand (O-H 1.004–1.019 Å, H...Cl 1.936–2.000 Å, O...Cl 2.847–2.896 Å, O-H...Cl 142.0–148.2°). These values meet the expectations.²³

Table 6. Selected Structural Parameters of Hydroxycarbene Complexes $[\text{PtCl}_2\text{X}\{\text{C}(\text{OH})\text{Et}\}]^n$ (bond lengths in Å, angles in deg)

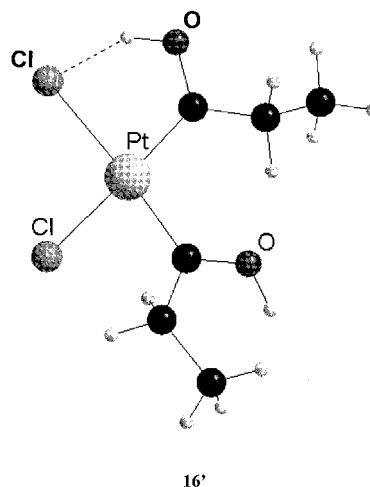
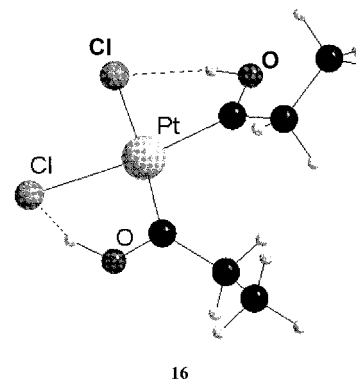
	17	15	16	16' ^a	18	11 ^b
X	Cl	C=CHMe	C(OH)Et	C(OH)Et	MeC≡CH	C(O)Et
n	1-	0	0	0	0	1-
Pt=C/BO ^c	1.939/0.935	2.004/0.800	1.982/0.810 1.982/0.810	1.984/0.799 1.936/0.826	1.985/0.775	1.967/0.844
C-O/BO ^c	1.316/1.255	1.292/1.330	1.294/1.354 1.296/1.355	1.295/1.354 1.312/1.259	1.298/1.340	1.286/1.372
Pt=C-C	128.2	127.3	128.8/129.6	128.7/122.4	128.1	123.8
Pt=C-O	121.9	120.9	119.7/119.5	120.8/120.6	121.2	122.9
C-C-O	109.9	111.8	111.3/110.5	110.4/116.8	110.7	113.3
O-H	1.004	1.013	1.015/1.012	1.019/0.981	1.009	1.077
H...Cl	2.000	1.979	1.961/1.994	1.936	1.993	
O...Cl	2.896	2.876	2.847/2.860	2.853	2.880	
O-H...Cl	147.3	146.1	144.3/142.0	148.2	145.2	
Pt-Cl _{trans}	2.404	2.373	2.424/2.427	2.397/2.438	2.379	2.458
Pt-Cl _{cis}	2.371/2.425	2.401	2.427/2.424	2.438/2.397	2.377	2.491
Cl-Pt-Cl	89.5/89.5	90.7	88.6	89.7	90.1	87.1
C-C-O/PtCl ₂	5.9/6.8	5.2	20.7/25.6	4.4/61.8	3.7	23.8

^a First values refer to hydrogen-bonded hydroxycarbene ligand and second values to non-hydrogen-bonded ligand. ^b For comparison the hydroxycarbene part of platina- β -diketone unit in complex **11** is given. ^c Bond orders (given in electron pairs).

**Figure 4.** Calculated structure of hydroxycarbene complex $[\text{PtCl}_3\{\text{C}(\text{OH})\text{Et}\}]^-$, **17**.

These hydrogen bondings give rise to a nearly coplanar complex and hydroxycarbene ligand planes (C-C-O/PtCl₂ 3.7–6.8°) in complexes **15**, **17**, and **18**. In bis(hydroxycarbene) complex **16** (Figure 5), formation of two O-H...Cl bridges results in (slight) tetrahedral distortion of the PtCl₂C₂ complex plane (Cl-Pt-C 173.0/172.5°). Isomeric complex **16'** (Figure 5), containing only one O-H...Cl bridge, is 7.0 kcal/mol higher in energy than complex **16** but less distorted from planar coordination (Cl-Pt-C 176.2/176.4°). As for other complexes with only one hydroxycarbene ligand (**15**, **17**, **18**), the hydrogen-bonded hydroxycarbene ligand lies nearly in the complex plane (C-C-O/PtCl₂ 4.4°). The non-hydrogen-bonded hydroxycarbene ligand includes with the complex plane an angle of 61.8°.

Complex **16'** allows the comparison of hydrogen- and non-hydrogen-bonded hydroxycarbene ligands. Formation of a O-H...Cl bridge gives rise to a shortening of the C-O bond (1.295 vs 1.312 Å) and lengthening of Pt=C (1.984 vs 1.936 Å) and Pt-Cl bonds (2.438 vs 2.397 Å). In all complexes (including **16'**) coordination of hydroxycarbene to platinum results in shortening of the C-O bond (1.292–1.316 vs 1.330 Å in noncomplexed hydroxycarbene calculated at the same level of theory). Formation of O-H...Cl bridges gives rise to

**Figure 5.** Calculated structures of two isomeric complexes $[\text{PtCl}_2\{\text{C}(\text{OH})\text{Et}\}_2]$ **16** and **16'** with two and one O-H...Cl hydrogen bonds, respectively.

marked lengthening of the O-H bonds (1.004–1.015 vs 0.973–0.981 Å in noncomplexed hydroxycarbene and in non-hydrogen-bonded hydroxycarbene ligand in **16'**).

Due to the hydrogen bonding to cis standing chloro ligands, in all hydroxycarbene complexes described here the metal fragment and the hydroxyl hydrogen are positioned syn (*Z*-isomer). The non-hydrogen-bonded

(23) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1993. (b) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1994.

Table 7. Electronic and Energetic Balance for the Hydroxycarbene Complex Formation

reaction	co-ligand	total charge	$q(\text{C}_\alpha)^a$	$q(\text{C}_\beta)^a$	ΔE in kcal/mol
12 \rightarrow 17	Cl	1-	0.141	-0.449	-45.6
14 \rightarrow 15	C=CHMe	0	0.146	-0.402	-51.3
15 \rightarrow 16	C(OH)Et	0	0.138	-0.407	-44.0
21 \rightarrow 11	C(O)Et	1-	0.125	-0.451	-52.3

^a Charge on α - and β -C atoms of starting vinylidene complexes (given in electrons).

Table 8. Selected Structural Parameters of Acyl Complexes [PtCl₂X{C(O)Et}]ⁿ (bond lengths in Å, angles in deg)

	19	20	21	11^a
X	Cl	MeC \equiv CH	C=CHMe	C(OH)Et
n	2-	1-	1-	1-
Pt-C/BO ^b	1.964/0.800	2.012/0.695	2.046/0.635	2.001/0.771
C=O/BO ^b	1.227/1.722	1.222/1.768	1.216/1.807	1.253/1.482
Pt-C-C	115.1	118.8	117.2	121.4
Pt-C=O	126.8	121.8	122.6	122.7
C-C=O	118.2	119.4	120.2	115.8
Pt-Cl _{trans}	2.590	2.533	2.511	2.491
Pt-Cl _{cis}	2.431/2.431	2.385	2.400	2.458
Cl-Pt-Cl	91.8/91.8	91.9	91.9	87.1
C-C=O/PtCl ₂	88.5/88.6	56.3	65.7	26.8

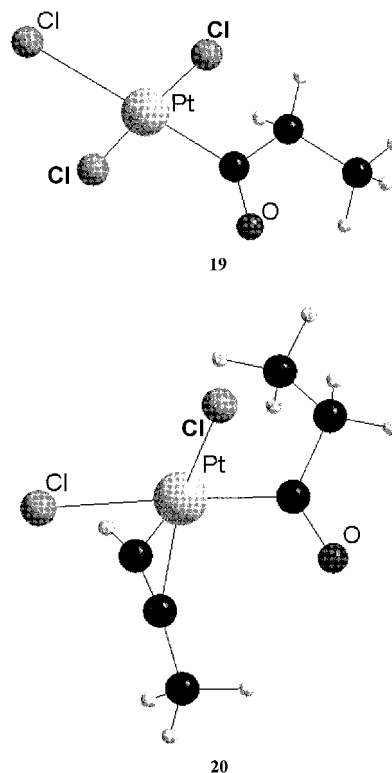
^a For comparison the acyl part of platina- β -diketone unit in complex **11** is given. ^b Bond orders (given in electron pairs).

hydroxycarbene ligand in **16'** exhibits an anti (*E*) conformation. In the literature, hydroxycarbene complexes with syn (*Z*) and anti (*E*) conformation are described. The preferred conformation seems to be strongly determined by hydrogen bonding between the OH proton and an H acceptor.²⁴ As found in complexes **15**–**18**, hydrogen bonding O–H \cdots X (X = halo ligand in cis position) was also verified experimentally.²⁵

Addition of water to vinylidene complexes results in formation of hydroxycarbene complexes (reaction type c, Table 1). These reactions are strongly exothermic in all cases (–44.0 to –52.3 kcal/mol) (Table 7). Reaction energies do not depend on the total charge of the vinylidene complex. Furthermore, reaction energies do not correlate with charges on α -C or β -C of the vinylidene moiety at which OH[–] and H⁺, respectively, is added (Table 7). This points to orbital control of these reactions and might be indicative for thermodynamic control of these reactions.

3.6. Acyl Complex Formation. Selected structural parameters of acyl complexes calculated in this work are given in Table 8. As examples, structures of acyl complexes **19** and **20** are shown in Figure 6. In complex **19** the plane of the acyl ligand is perpendicular to the complex plane (C–C–O/PtCl₂ 88.6°). In complexes **20** and **21** the stronger π -acidic co-ligands (MeC \equiv CH, **20**; C=CHMe, **21**) are perpendicular to the complex planes, whereas the angles between the acyl ligands and the complex plane are 56.3° (**20**) and 65.7° (**21**), respectively.

Acyl complexes are generated by deprotonation of hydroxycarbene complexes. Here, energies of reactions

**Figure 6.** Calculated structures of acyl complexes [PtCl₃{C(O)Et}]^{2–}, **19**, and [PtCl₂{C(O)Et}(η^2 -MeC \equiv CH)][–], **20**.

between hydroxycarbene complexes and hydroxide ions are calculated (reaction type d, Table 1) to avoid the formation of protons being highly energetic in the gas phase. Reactions starting from neutral hydroxycarbene complexes **15** and **18** are highly exothermic (**15** \rightarrow **21** –122.2 kcal/mol; **18** \rightarrow **20** –121.1 kcal/mol). This effect can be ascribed to a benefit from charge delocalization and formation of a C=O double bond. Analogous reaction of complex **16** yielding platina- β -diketone **11** is even more exothermic (–130.4 kcal/mol), most likely due to additional formation of a strong O–H \cdots O hydrogen bridge.

Even deprotonation of **17**, yielding the dianionic acyl complex **19** is exothermic (–28.8 kcal/mol). But it is less exothermic by about 100 kcal/mol than deprotonations yielding monoanionic acyl complexes previously described, obviously due to high charge density in complex **19**. Nevertheless, when formation of a doubly negatively charged complex (**17** \rightarrow **19**) is exothermic, even in the gas phase, it should be preferred thermodynamically much more in solution of a polar solvent.

For deprotonation of hydroxycarbene complexes with cis standing chloro ligands another pathway has to be discussed (reaction type d', Table 1), namely, HCl elimination that was also experimentally observed.^{16b,17d} Thus, instead of the reaction sequence **17** \rightarrow **19** \rightarrow **20**, cleavage of HCl from hydroxycarbene complex **17** could provide a coordinatively unsaturated platinum complex **19'** that reacts with propyne yielding intermediate complex **20** (Figure 7). Reaction **17** \rightarrow **19'** is weakly endothermic ($\Delta E = 7.9$ kcal/mol), but it is exergonic ($\Delta G^\circ = -7.6$ kcal/mol) due to strong entropy influence. On the basis of the present results neither of the two pathways can be excluded. But the preference of route C over routes A and B (cf. Figure 1) is out of the question

(24) (a) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1981**, *20*, 34. (b) Motz, P. L.; Ho, D. M.; Orchin, M. *J. Organomet. Chem.* **1991**, *407*, 259. (c) Knox, J. R.; Prout, C. K. *Acta Crystallogr.* **1969**, *25B*, 1952.

(25) (a) Moss, J. R.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 975. (b) Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1979**, *171*, 65. (c) Casey, C. P.; Sakaba, H.; Underiner, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 6673.

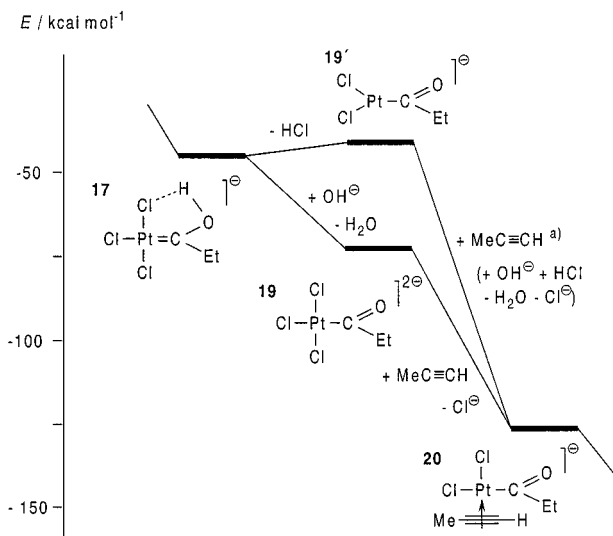
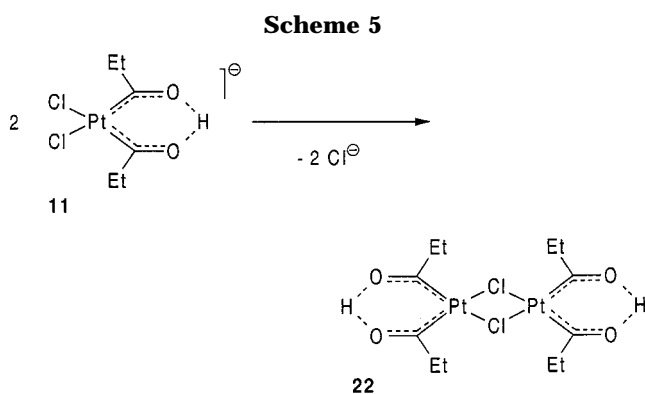


Figure 7. Reaction pathways for deprotonation of hydroxycarbene complex **17**: addition of OH^- vs cleavage of HCl . ^aReaction **19'** \rightarrow **20** includes addition of $\text{MeC}\equiv\text{CH}$ (-2.7 kcal/mol) and neutralization $\text{OH}^- + \text{HCl}$ (-87.0 kcal/mol).



because in the alternative routes the strongly endothermic steps (route A, **12** \rightarrow **13**; route B, **17** \rightarrow **18**) lie before the deprotonation of a hydroxycarbene moiety.

$[\text{PtCl}_2\{\text{C}(\text{O})\text{Et}\}]^-$, **19'**, is a planar, distorted T-shaped complex ($\text{Cl}-\text{Pt}-\text{C}$ $95.5/97.4^\circ$, $\text{Cl}-\text{Pt}-\text{Cl}$ 167.0°). The acyl ligand is nearly perpendicular to the complex plane ($\text{C}-\text{C}=\text{O}/\text{PtCl}_2$ 81.0°).

3.7. Formation of Dinuclear Platina- β -diketone.

Two equivalents of mononuclear platina- β -diketonate anion **11** react with cleavage of chloro ligands yielding the dinuclear platina- β -diketone **22** (Scheme 5). Structures and selected structural parameters of complexes **11** and **22** are shown in Figure 8 and Table 9. In both complexes, platinum possesses a normal planar geometry. In dinuclear complex **22** the Pt_2Cl_2 four-membered ring is puckered with a dihedral angle $\text{Pt}-\text{Cl}-\text{Cl}-\text{Pt}$ of 166.3° . The platina- β -diketone units are not planar. The planes of acyl and hydroxycarbene ligands include complex plane angles between 14.7 and 17.4° (**22**) and $23.8/26.3^\circ$ (**11**). Starting with a hypothetical planar arrangement, the motion of acyl and hydroxycarbene moieties had been disrotatory.

Solid state structure of complex **22**²⁶ shows a good agreement with the calculated one (Table 9). Two facts

(26) Heinemann, F. W.; Gerisch, M.; Steinborn, D. Z. *Kristallogr. NCS* **1997**, *212*, 181.

are to be mentioned: Like the methyl and 4-phenylbutyl analogues $[\text{Pt}_2(\mu\text{-Cl})_2\{(\text{COR})_2\text{H}\}_2]$ ($\text{R} = \text{Me}, (\text{CH}_2)_4\text{Ph}$),² the ethyl complex ($\text{R} = \text{Et}$) exhibits a planar Pt_2Cl_2 rhomboid unit with crystallographic imposed C_i symmetry. The platina- β -diketone units are planar or less bent than those in calculated structure **22** (interplanar angles between acyl/hydroxycarbene moieties and complex planes are 1.0 – 6.2°). Otherwise, the platina- β -diketone unit in the mononuclear complex $[\text{PtCl}\{(\text{COMe})_2\text{H}\}(\text{quin})]$ (quin = quinoline) was found to be nonplanar, with angles of 16.1° and 13.0° between the complex plane and planes of the acyl/hydroxycarbene ligands.²⁷ Detailed calculations of $[\text{Pt}_2(\mu\text{-Cl})_2\{(\text{COR})_2\text{H}\}_2]$ ($\text{R} = \text{H}, \text{Me}$) in dependence on symmetry showed that the energy of the complexes does not depend strongly on the bending of the platina- β -diketones unit.²⁸

$\text{O}-\text{H}\cdots\text{O}$ hydrogen bridges in platina- β -diketones **11** and **22** were calculated to be nonsymmetrical. Thus, a hydroxycarbene and acyl part can be formally distinguished. Comparison of hydroxycarbene and acyl moieties in platina- β -diketone complex **11** with hydroxycarbene complexes (Table 6) and acyl complexes (Table 8) exhibits significant stabilization of the hydroxycarbene unit by hydrogen bonding at the expense of the acyl part.

The values of $d(\text{Pt}-\text{Cl}_{\text{trans}})$ ²⁹ in complexes $[\text{PtCl}_3\text{R}]^n$ ($n = 1-, 2-$) (**10**, **12**, **17**, **19**) reflect the (structural) trans-influence of ligand R.³⁰ From this the following (structural) trans-influence series was obtained: $-\text{C}(\text{O})\text{Et} > \text{C}(\text{OH})\text{Et} > \text{C}=\text{CHMe} > \text{MeC}\equiv\text{CH}$. The same series was obtained by evaluating $\text{Pt}-\text{Cl}_{\text{trans}}$ in the complexes $[\text{PtCl}_2\text{RR}]^n$ ($n = 0, 1-$). Considering mononuclear platina- β -diketone complex $[\text{PtCl}_2\{(\text{COEt})_2\text{H}\}]^-$, **11**, it will be obvious that “acyl” and “hydroxycarbene” moieties in the platina- β -diketone unit have a lower trans-influence than the acyl ligand (2.491 Å in **11** vs 2.511 – 2.590 Å in **19**–**21**,³¹ cf. Table 8) and a higher trans-influence than the hydroxycarbene ligand (2.458 Å in **11** vs 2.373 – 2.404 Å in **15**–**18**,³² cf. Table 6), respectively. This is exactly what is expected when the acyl part becomes “hydroxycarbene-like” and vice versa due to intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding.

Dimerization according to Scheme 5 is strongly endothermic (57.4 kcal/mol).³³ This is mainly caused by two facts: (i) Generation of Cl^- is accompanied with a loss of charge delocalization and (ii) the net balance of broken and formed bonds is unfavorable because terminal $\text{Pt}-\text{Cl}$ bonds are stronger than bridging ones. The thermodynamics of the formation of the dinuclear complex is expected to be reversed by solvation and eventually also by entropy effects. Nevertheless, the energy demand for dimerization will be overcompensated by the strong exothermic formation of the mono-

(27) Gerisch, M.; Heinemann, F. W.; Bruhn, C.; Scholz, J.; Steinborn, D. *Organometallics* **1999**, *18*, 564.

(28) Maulitz, A.; Nordhoff, K.; Steinborn, D., unpublished.

(29) Normalized to $d(\text{Pt}-\text{Cl}_{\text{cis}})$. The $\text{Pt}-\text{Cl}_{\text{trans}}$ bond of complex **17** was normalized to the $\text{Pt}-\text{Cl}_{\text{cis}}$ bond that is not elongated by the $\text{O}-\text{H}\cdots\text{Cl}$ bond.

(30) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(31) Bond lengths $\text{Pt}-\text{Cl}_{\text{trans}}$ are given.

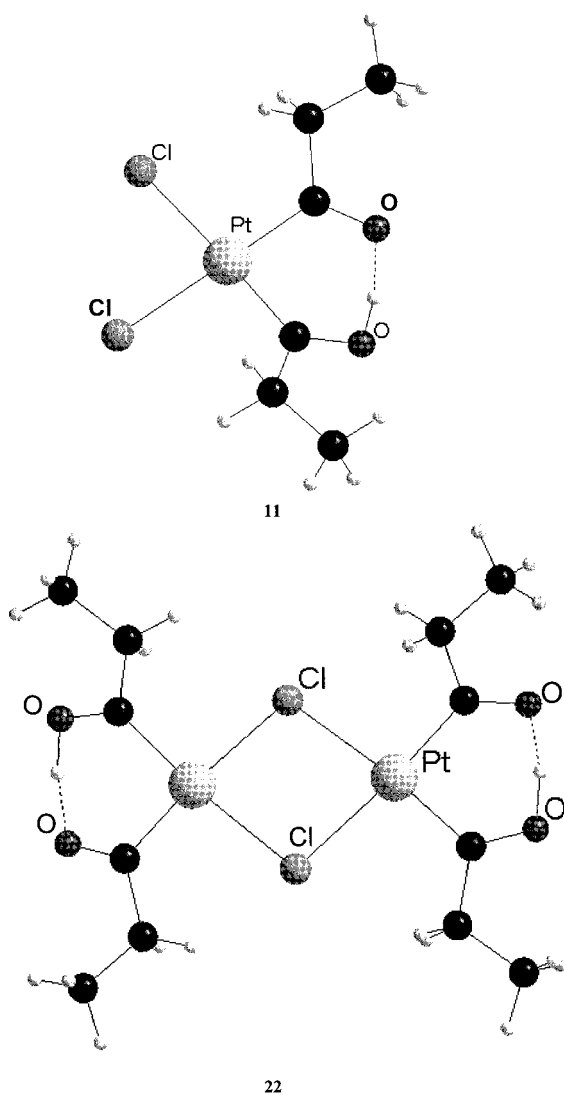
(32) $\text{Pt}-\text{Cl}$ bonds that are elongated by $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds were not considered.

(33) The size of the dimeric platina- β -diketone **22** did not allow zero-point correction; hence only the value without zero-point correction could be given.

Table 9. Selected Structural Parameters of Mononuclear (**11**) and Dinuclear Platina- β -diketones (**22**) and Comparison with Experimental Values of $[\text{Pt}_2(\mu\text{-Cl})_2\{(\text{COR})_2\text{H}\}_2]$ (R = Me, Et) (bond lengths in Å, angles in deg)

	$[\text{PtCl}_2\{(\text{COEt})_2\text{H}\}]^-$	$[\text{Pt}_2\text{Cl}_2\{(\text{COEt})_2\text{H}\}_2]$	$[\text{Pt}_2(\mu\text{-Cl})_2\{(\text{COR})_2\text{H}\}_2]$	
	11	22	R = Me	R = Et
Pt–C/BO	2.001/0.771	1.995/0.796	1.95(1)	1.97(1)
C=O/BO	1.253/1.482	1.245/1.592	1.23(1)	1.23(1)
Pt=C/BO	1.967/0.844	1.966/0.852	1.95(1)	1.96(1)
C–O/BO	1.286/1.372	1.274/1.422	1.26(1)	1.25(1)
C–Pt–C	90.2	91.2	91.4(5)	90.3(4)
O–H	1.077	1.085		
H \cdots O	1.357	1.355		
O \cdots O	2.405	2.411	2.37(1)	2.41(2)
O–H \cdots O	162.0	162.6		
Pt–Cl ^a	2.458	2.508	2.430(4)	2.449(3)
Pt–Cl ^b	2.491	2.560	2.430(3)	2.460(3)
Cl–Pt–Cl	87.1	80.1	80.7(1)	79.4(1)
C–C–O/PtCl ₂ ^c	–23.8	–14.9/–14.7	–1.0	–6.2
C–C=O/PtCl ₂ ^c	26.3	17.4/17.1	3.3	5.6

^a Trans to hydroxycarbene moiety. ^b Trans to acyl moiety. ^c Different signs of interplanar angles were used to point out that the motion had been disrotatory.

**Figure 8.** Calculated structures of platina- β -diketonate complexes $[\text{PtCl}_2\{(\text{COEt})_2\text{H}\}]^-$, **11**, and $[\text{Pt}_2(\mu\text{-Cl})_2\{(\text{COEt})_2\text{H}\}_2]$, **22**.

nuclear platina- β -diketone **11**, and the resulting value for the formation (in gas phase) of **22** from **10** can be estimated to be about -296 kcal/mol.

3.8. Discussion. Formation of anionic mononuclear platina- β -diketone complex **11** from the propyne complex analogous to Zeise's anion **10** can be assumed to proceed via alkyne–vinylidene equilibration, substitution of Cl^- by propyne, addition of water to the vinylidene ligand yielding a hydroxycarbene unit, and its deprotonation, affording an acyl ligand (Table 1). These elementary reactions can be combined in three reasonable reaction pathways that are shown in Figure 1. Routes A and B are connected with one strongly endothermic step (**12** \rightarrow **13**, $+42.1$ kcal/mol; **17** \rightarrow **18**, $+39.3$ kcal/mol), namely, the substitution of Cl^- by propyne. The corresponding reaction in route C is strongly exothermic (**19** \rightarrow **20**, -53.0 kcal/mol) because the substitution proceeds at a doubly negatively charged complex. Apart from the nearly thermoneutral alkyne–vinylidene tautomerization (<2 kcal/mol), all reactions of route C are strongly exothermic (-28.8 to -53.0 kcal/mol).

Analysis exhibits that elementary steps seem not to be markedly charge controlled. This points to thermodynamic control of reactions, and the Hammond principle should be valid. No reaction barriers were calculated within this study, not even for the nearly thermoneutral π -alkyne–vinylidene tautomerization processes. Because they are an immanent part of all three reaction pathways, they should not give preference for one of them. Thus, routes A and B have to be abandoned in favor of route C. All calculations were done in the gas phase, neglecting any solvent influences.

The reaction scheme in Figure 1 is simplified insofar as there are other routes to go from complex **10** to complex **11**. For instance, routes B/C and A/C are connected via deprotonation reactions **18** \rightarrow **20** and **15** \rightarrow **21**, respectively. But, they do not need to be considered, because they lie after the crucial endothermic steps. Another pathway cannot be ruled out, namely, the formation of dinuclear complexes at an early stage of the reaction. When the reaction starts from the propyne complex analogous to Zeise's dimer, $[\text{Pt}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^2\text{-MeC}\equiv\text{CH})_2]$, it can be expected—taking into consideration the same arguments as above—that the reaction proceeds in analogy to route C (deprotonation of hydroxycarbene before substitution of Cl^- by propyne).

Noted Added in Proof. To estimate the influence of a solvent (methanol) on the energetics of individual steps, we performed single-point PCM calculations on gas-phase optimized structures of crucial species. Consideration of solvent results in less endothermic steps in pathways A and B than is the case in the gas phase. Nevertheless, these preliminary investigations indicate the pathway C to be thermodynamically preferred over pathways A and B also in solution, quite similar to that found in the gas phase. The influence of solvent on the mechanism will be clarified in further investigations.

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Supporting Information Available: Complete tables of Cartesian coordinates of atom positions calculated for **10–22**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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