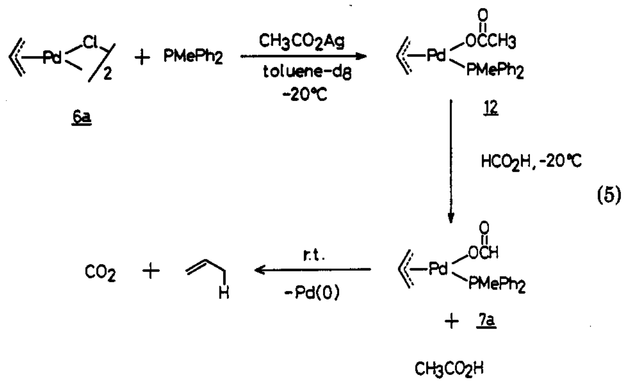
allylic acetate into terminal olefins is the feasibility of the displacement of the acetate group by the formate group. For an examination of the process, the (π-allyl)(diphenylmethylphosphine)palladium acetate complex **12** was prepared by a process similar to that employed for the formate complex **7a** with the use of silver acetate instead of silver formate in eq 5.[14] Spectroscopic examination of the change of the ^1H NMR spectrum on addition of formic acid to the toluene solution containing **12** indeed indicated the displacement of the acetate ligand by the formate ligand with liberation of acetic acid and production of the (π-allyl)palladium formate complex **7a** at −20 °C. Warming the solution led to liberation of propene, as was observed in the thermal decomposition of the isolated complex **7a**.



In conclusion, key intermediate complexes shown in Scheme I, except for the (π-allyl)palladium hydride complex **4**, which apparently is quite unstable,[15] have been identified in the present study in support of the validity of the proposed reaction mechanism. The influence of tertiary phosphine ligands on the course of reductive cleavage of the allylic substrates is presently under investigation.

Registry No. **6a**, 12012-95-2; **6b**, 132884-87-8; **7a**, 132884-83-4; **7b**, 132884-84-5; **7c**, 132884-85-6; **7d**, 132884-86-7; **8a**, 1838-59-1; **8b**, 132884-82-3; **8c**, 820-57-5; **9** (L = $PMePh_2$), 132957-78-9; **9** (L = PMe_3), 132957-79-0; **11a**, 132884-89-0; **11b**, 132884-91-4; **11c**, 132884-93-6; **12**, 132884-94-7; 1-butene, 106-98-9; 2-butene, 624-64-6; styrene, 100-42-5.

---

[14] NMR spectra of **12**: ^1H NMR (400 MHz, toluene-d_8, −20 °C) δ 5.07 (m, 1 H, H_c), 4.49 (t, J = 7.0 Hz, 1 H, R = H), 3.77 (dd, J = 13.9, 9.5 Hz, 1 H, H_d), 2.51 (dd, J = 13.2, 7.0 Hz, 1 H, H_b), 2.18 (b s, 3 H, CH_3CO_2−).

[15] For an analogous (π-allyl)platinum hydride formation of propene has been confirmed: Bertani, R.; Carturan, G.; Scrivanti, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 246.

Aqueous Organometallic Chemistry: Synthesis and Structure of Chloro[(1–3-η:6–8-η)-2,7-dimethyloctadienediyl](semicarbazide)ruthenium(IV) Chloride Dihydrate

Shaun O. Sommerer and Gus J. Palenik*

Center for Molecular Structure, Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received December 19, 1990

Summary: The first example of a water-soluble cationic Ru(IV) complex with two η^3-allyl functions has been isolated and characterized by an X-ray crystal structure study. The Ru ion is at the center of a distorted trigonal bipyramid where the equatorial donors are two η^3-allyl functions and a terminal semicarbazide N. The O of the semicarbazide and Cl reside in the axial positions.

We wish to report our discovery and characterization of a unique cation that can provide a convenient entry into aqueous high formal oxidation state organometallic chemistry. There is current interest in both water-soluble organometallic compounds for various catalytic reactions[1] and organometallic compounds with high formal oxidation states.[2] Organometallic compounds were generally considered to require low formal oxidation states, but this perception is disappearing. The recent discovery of an aqueous ring-opening metathesis polymerization reaction[3] is only one of the new areas of aqueous organometallic chemistry, even though the species involved were neither isolated nor identified.

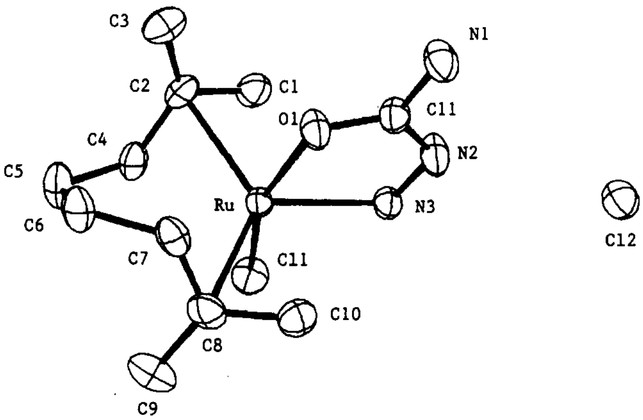


Figure 1. View of chloro[(1–3-η:6–8-η)-2,7-dimethyloctadienediyl](semicarbazide)ruthenium(IV) chloride showing the atomic numbering with the thermal ellipsoids drawn at the 50% probability level.

As part of a continuing study of the reactions of DAPSC, 2,6-diacetylpyridine-disemicarbazone, with various metal ions of the second and third row,[4] we reacted DAPSC with

---

* To whom correspondence should be addressed.

[1] Fache, E.; Senocq, F.; Santini, C.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1990**, 1776. Chan, T. C.; Li, C.-J. *Organometallics* **1990**, *9*, 2649. Light, J.; Breslow, R. *Tetrahedron Lett.* **1990**, *31*, 2957 and references therein.

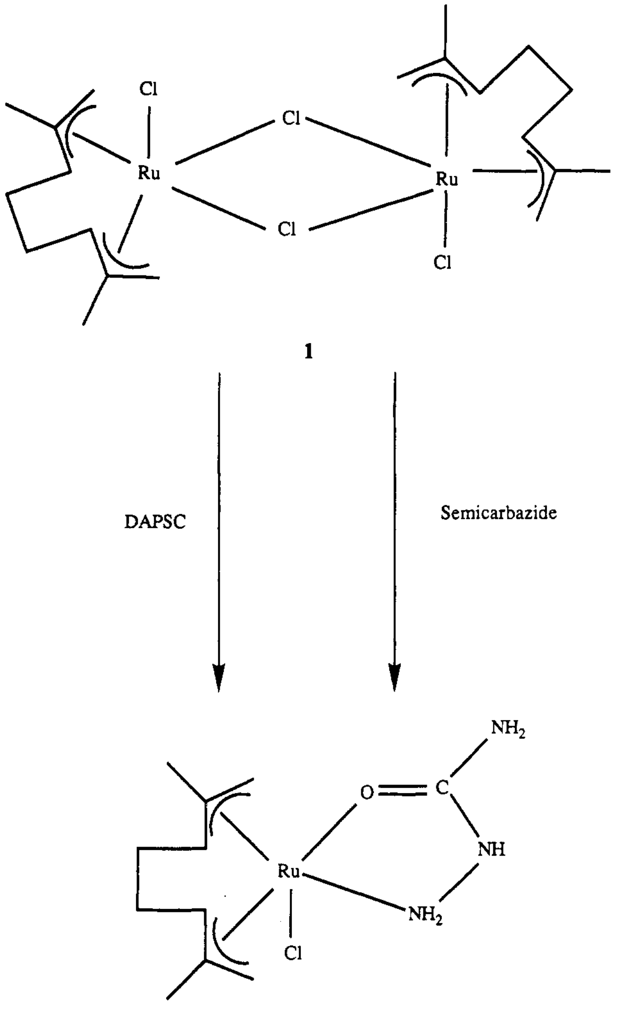
[2] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297. Herrmann, W. A. *Comments Inorg. Chem.* **1988**, 73.

[3] Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

[4] Wester, D. W.; Palenik, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 6505. Wester, D. W.; Palenik, G. J. *J. Am. Chem. Soc.* **1974**, *96*, 7576. Palenik, G. J.; Wester, D. W.; Rychlewska, U.; Palenik, R. C. *Inorg. Chem.* **1976**, *15*, 1814. Thomas, J. E.; Palenik, G. J. *Inorg. Chim. Acta* **1980**, *44*, L303. Thomas, J. E. M.S. Dissertation, University of Florida, Gainesville, FL, 1980.

0276-7333/91/2310-1223$02.50/0

Scheme I



2

bis(μ-chloro)bis[(2,7-dimethylocta-2,6-diene-1,8-diyl)ruthenium(IV)] chloride (1). The unexpected result was the first example of a water-soluble cationic Ru(IV) π-allyl complex, 2 (see Scheme I). The crystals are air-stable and water-soluble and decompose at 180 °C. The reactions of 1 have not been extensively studied, although a recent report postulated the existence of cationic Ru(IV) species.[5]

The yield of 2 can be increased dramatically by the reaction of 1 with semicarbazide hydrochloride. For example, 50 mg (0.08 mmol) of 1 was combined with 18.1 mg (0.16 mmol) of semicarbazide hydrochloride in deionized water (pH 1.50) and heated to 55 °C for 2 h. A clear yellow-brown solution formed, which was filtered and cooled to room temperature (25 °C). Slow evaporation of this solution produced brown crystals of 2 in 77% yield.[6]

The cation, together with the ionic chloride, is shown in Figure 1. The geometry around the Ru(IV) ion is that of a distorted trigonal bipyramid, with the two most electronegative elements in the axial positions. An electron count indicates that the Ru ion has an inert-gas configuration or satisfies the 18-electron rule. The O(1)–Ru–N(3) angle is only 77.3 (1)°, which is typical of semicarbazide chelate rings and other five-membered chelate rings.[4,8] The corresponding O(1)–Ru–Cl(1) angle is 159.70 (8)°, which is considerably less than 180°. The nonlinearity is a consequence of the small chelate angle plus some steric interactions with the diene.

Several important conclusions and observations can be made from our results. First, the water solubility of 2 is unprecedented in π-allyl compounds, particularly of Ru(IV).[9] Second, the unusual cleavage of the DAPSC ligand suggests that reactions of 1 with Schiff bases may yield hydrolysis products of the Schiff base, not the expected complex. Finally, water-soluble Ru(IV) species similar to 2 may exist in other aqueous $RuCl_3$ solutions with unsaturated organic molecules. The existence of 2 offers the potential for development of a water-based organometallic chemistry. The reactions of the dimer 1 with other bidentate ligands together with a study of the reactions of and possible catalytic activity of 2 are planned.

Acknowledgment. We wish to thank the NSF Instrumentation Program for a grant for the purchase of the Nicolet diffractometer.

Supplementary Material Available: Tables of crystal data, final positional and thermal parameters, hydrogen atom parameters, and distances and angles (5 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

---

(5) Cox, D. N.; Roulet, R. *Inorg. Chem.* **1990**, *29*, 1360.

(6) The brown crystals of $RuC_{11}N_3O_3H_{25}Cl_2$ (Anal. Found (calcd): C, 31.30 (31.50); H, 6.20 (6.01); N, 9.91 (10.02)) are triclinic (space group $P\bar{1}$, No. 2) with a = 7.1907 (12) Å, b = 15.280 (4) Å, c = 7.8244 (21) Å, α = 90.305 (22)°, β = 102.154 (18)°, γ = 89.895 (18)°, V = 840.4 (5) Å^3, Z = 2, D_c = 1.66 g/cm^3, and μ(Mo Kα) = 26.1 cm^{-1}. All measurements were made at room temperature (27 °C) with use of a Nicolet R3m diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71069 Å). The intensity crystal was 0.05 × 0.07 × 0.13 mm so that no absorption corrections were deemed necessary. After merging, the 2603 reflections with $F_0 \geq 2.5\sigma(F_o)$ were used in the analysis. Refinement by least-squares methods led to R = 0.027 and R_w = 0.034. All calculations were carried out with use of the PC version of NRCVAX.[7]

(7) Gabe, E. J.; Page, Y. L.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *23*, 384.

(8) Bhattacharya, S.; Chakravorty, A.; Cotton, F. A.; Mukherjee, R.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 1709 and references therein.

(9) Stable π-allyl complexes of Ru(IV) have been reported in ref 10 but are air- and water-sensitive.

(10) Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799. Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3887. Albers, M. O.; Liles, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2347 and references therein.