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Discovery of the First Metallaquinone

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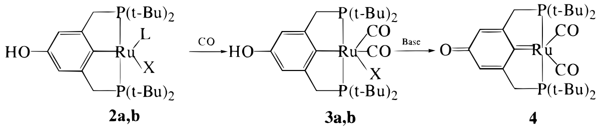
Quinoid systems such as quinones, quinone methides, quinodimethanes, and quinodiimines have been widely investigated regarding their chemical, biological, and physical properties.[1] Of special interest are their utility as charge transfer complexes due to the relatively low energy barrier between the ground and excited states. Some metal stabilized quinone methides have also been reported recently.[2] Remarkably, no metallaquinone, that is, a compound in which one of the oxygen atoms of a quinone has been replaced by a metal, has hitherto been reported. Such a compound is expected to have a strong dipolar contribution to the excited state compared to its biradical nature in quinones. We know of only one example of a stable quinoid compound which contains a heavier element (phosphorus)[3] instead of the oxygen.

We report here the synthesis and structure of the first stable metallaquinone. In this compound one of the oxygen atoms of the *p*-quinone system is replaced by ruthenium. This compound interconverts between a quinoid-Ru(0) carbene form in nonpolar solvents and a Ru(II)-quinolate zwitterionic form in polar solvents. Ru(0) carbenes are rare.[4]

As none of the methods for either the preparation of organic quinoid structures or of ruthenium(II) carbene systems[5] was suitable for our purpose, we designed a new synthetic pathway (Scheme 1). Reaction of the new phenolic PCP ligand 3,5-bis-(di-*tert*-butylphoshinomethylene)phenol (**1**),[6] with either $\mathrm{Ru(O_2CCF_3)_2CO(PPh_3)_2{\cdot}CH_3OH}$,[7] or $\mathrm{Ru(DMSO)_4Cl_2}$[8] in the presence of two equivalents of $\mathrm{NEt_3}$, results in a facile cyclometalation process, similar to the one previously reported,[9] forming **2a** and **2b**, respectively, in high yields. Bubbling CO through solutions

Scheme 1

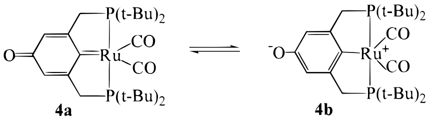


a: L= CO, X=TFA. **b**: L=$\mathrm{NEt_3}$, X=Cl   Base= KOH or Proton Sponge or Dabco

of **2a** and **2b** quantitatively produced the dicarbonyl complexes **3a** and **3b**, respectively.

Deprotonation of **3a** and **3b** with an equimolar amount of KOH in THF, at 25 °C overnight, or with 1,8-bis(dimethylamino)-naphthalene (Proton Sponge) or 1,4-Diazabicyclo[2.2.2]octane (Dabco), upon refluxing in methanol for 4 days, cleanly produced **4**. The presence of two strong π-acceptor CO ligands is essential for the charge transfer from the phenoxide moiety to the metal center, stabilizing the Ru(0)-metallaquinone formed. For comparison, addition of $\mathrm{PMe_3}$ to **2a** followed by deprotonation results in decomposition.

Complex **4** was characterized spectroscopically.[10] Significantly, some of its spectral characteristics are solvent-dependent. IR of a benzene solution shows three significant absorption signals at 1670, 1617, and 1586 $\mathrm{cm^{-1}}$ which are characteristic to C═O and C═C absorptions of quinoid systems, while these signals are absent in a methanol solution. The color of the benzene solution is reddish-orange, whereas the methanol solution is yellow. The UV−vis spectrum clearly supports this observation as in benzene there is one absorption signal at $\lambda_{\max} = 450$ nm ($\epsilon = 35\,400$) while in methanol there is a blue shift of the signal to $\lambda_{\max} = 432$ nm ($\epsilon = 22\,700$). ^{13}C NMR spectra recorded in different solvents shows even more dramatic changes. In THF-d_8 it exhibits signals at 303.08 ppm (characteristic for the C═Ru carbon of carbene complexes[5]) and at 187.45 ppm (characteristic for C═O carbon of quinones). In $\mathrm{CD_3OD}$ both these signals disappear and two new signals at 160.64 and 151.55 ppm are observed. In polar aprotic solvents (i.e. acetone) these signals are observed at 167.04 and 154.95 ppm. These observations led us to conclude that **4** appears in two different forms in different solvents, the quinoid form **4a** is present in less polar solvents such as benzene and THF and the zwitterionic form **4b** in polar solvents such as methanol and acetone. To the best of our knowledge, this type of zwitterionic organometallic compound is unprecedented.[11]



The structure of **4b**, which was crystallized from acetone solution by slow diffusion of diethyl ether, was confirmed by X-ray crystallography. The unit cell contains a molecule of Dabco (which was used as a base) per two molecules of **4b**. Comparison of the structures of **4b** and its precursor **3a** (Figure 1) shows similar bond lengths. The geometry around the ruthenium atom in **3a** is a distorted octahedron [OC−Ru−CO angle is 92.91-(14)°], while in **4b** it is a distorted square pyramid with the respective angle of 99.1(3)°.

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(10) IR (Film) 1983, 1921, 1659, 1590, 1577, 1030 $\mathrm{cm^{-1}}$. UV−vis-(benzene). $\lambda_{\max}= 450$ nm ($\epsilon = 35400$). ^{1}H NMR (THF-d_8, 250.2 MHz) 6.38 (s, 2H), 3.18 (br.s., 4H), 1.38 (t, 18H, $J_{\mathrm{P-H}} = 6.2$ Hz), 1.26 (t, 18H, $J_{\mathrm{P-H}} = 6.2$ Hz). ^{13}C NMR (THF-d_8, 100.6 MHz) 303.08 (t, $J_{\mathrm{P-C}} = 5.7$ Hz), 205.69 (t, $J_{\mathrm{P-C}} = 6.3$ Hz) 204.74 (t, $J_{\mathrm{P-C}} = 8.3$ Hz), 187.45 (s), 148.68 (t, $J_{\mathrm{P-C}} = 6.4$ Hz), 111.55 (t, $J_{\mathrm{P-C}} = 8.9$ Hz), 40.34 (t, $J_{\mathrm{P-C}} = 11.4$ Hz), 36.70 (m), 30.52 (s), 29.85 (s). ^{31}P {^{1}H} (THF-d_8, 101.3 MHz) 103.41 (s). The ν(CO) reported for $\mathrm{Ru(CF_2)(CO)_2(PPh_3)_2}$ in ref 4, 1983, 1910 $\mathrm{cm^{-1}}$, are very similar to those for **4a** (see above).

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10.1021/ja001759d CCC: $19.00

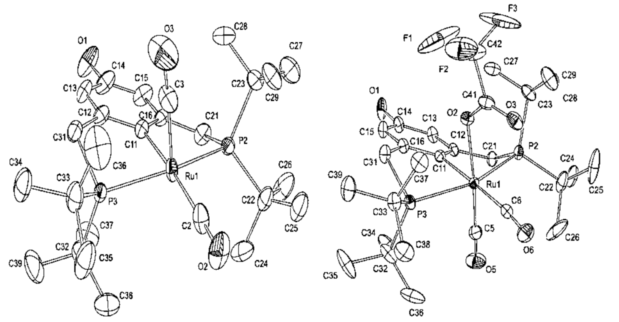

Figure 1. Elipsoid plots of complexes **4b** (left) and **3a** (right) Hydrogen atoms were omitted for clarity.[12]

High-level calculations have revealed some unique features regarding the structure and energetic properties of this system. All calculations were carried out using the Gaussian 98 program system.[13] B3LYP[14]/LANL2DZ[15] geometry optimizations and harmonic frequency calculations were carried out on a model compound for the full system **4a** (in which all tertiary butyl substituents were replaced by hydrogen atoms), while the full system was also studied by means of the ONIOM[16] (B3LYP/LANL2DZ:HF/LANL1MB[15]) approach. In both cases, three stationary points were found that are very similar in all respects relevant to this discussion: we will focus on the C_s structure which is marginally more stable than the others.

Clearly quinonic geometries were found, even when a "zwitterionic" starting geometry was used deliberately. For instance, the $C_{ipso}-C_{ortho}$, $C_{ortho}-C_{meta}$, and $C_{meta}-C_{para}$ bond lengths in **4a** are 1.463, 1.368, and 1.463 Å, respectively, at the ONIOM(B3LYP/LANL2DZP:[17]HF/LANL1MB) level, while the $C_{para}{=}O$ bond distance is 1.239 Å, much closer to the distances at that level of theory for quinone than for hydroquinone. The computed Wiberg bond order[18] for $C_{para}{=}O$ is 1.56 at the B3LYP/LANL2DZ level, and $C_{para}{=}O$ and $C_{ipso}{=}Ru$ bonds are clearly present in the natural bond orbital (NBO)[19] analysis. Summarizing, the computed gas-phase structure is clearly "quinonic" in character, as opposed to the clearly "zwitterionic" X-ray diffraction structure.

Aside from the C−H and CO ligand stretching frequencies, the ONIOM(B3LYP/LANL2DZP:HF/LANL1MB) computed IR spectra of **4a** have a number of "fingerprint" features in regions not masked by the *t*-Bu vibrations: (a) an intense $C_{para}{=}O$ stretch at 1689 cm^{-1}, (b) symmetric and antisymmetric combinations of the $C_{meta}{=}C_{para}$ stretches at 1624 and 1564 cm^{-1}, of which only the former is intense, and (c) the $C_{ipso}{=}Ru$ stretch at 1036 cm^{-1}. While the latter may seem surprising at first, we note that ω_e of the RuC diatomic is known[20] to be 1030 cm^{-1}. (c) is the first assignment of the absorption band of a Ru−carbene bond.

The experimental IR spectrum of neat **4a** has an intense band at 1030 cm^{-1} which would correspond to (c), and a triplet of intense bands at 1577, 1590, and 1659 cm^{-1} which are most easily explained as (a) and (b). We note that the C=O and symmetric $C_{ortho}{=}C_{meta}$ bands exhibit appreciable coupling in the computed spectrum, and therefore (a) and (b) are best considered together; we also note that at the level of theory concerned, reproduction of computed IR intensities will be semiquantitative at best: this should be kept in mind when comparing the computed intensities with the observed peak areas.

Computational limitations precluded treatment of the electronic spectrum of **4a**; however, since the essential structural and vibrational features found in **4a** are present in the model compound as well, we have carried out time-dependent density functional theory[21] calculations of its five lowest-lying electronic transitions. Only one band (514 nm) with a high oscillator strength is present in the visible range; it corresponds to an excitation from the Ru=C π HOMO into the ring π^* LUMO. Experimentally, indeed one peak (452 nm in C_6H_6, 432 nm in MeOH) is seen in the visible range.

By means of a constrained ONIOM (B3LYP/LANL2DZ:HF/LANL1MB) optimization on the model compound, we find that distortion to the zwitterionic structure (not a local minimum on the potential surface) requires about 13 kcal/mol.

In summary, we have prepared and characterized the first metallaquinone, which can be easily transformed into its zwitterionic form. This transformation is reversible. We are currently investigating the utility of this novel compound.

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Supporting Information Available: Text describing the synthesis and characterization of compounds **1**−**4** and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **3a** and **4b** and Cartesian coordinates of all computed compounds (PDF). This material is available free of charge via the Internet at http::/pubs.acs.org.

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(12) Relevant distances (Å) and angles (deg): **4b**: Ru(1)−C(11) 2.121(6); O(1)−C(14) 1.373(8); C(11)−C(12) 1.396(9); C(11)−C(16) 1.397(9); C(12)−C(13) 1.386(9); C(13)−C(14) 1.372(9); C(14)−C(15) 1.393(10); C(15)−C(16) 1.410(9); P(2)−Ru(1)−P(3) 157.46 (6); C(2)−Ru(1)−C(3) 99.1(3). **3a**: Ru(1)−C(11) 2.117(3); O(1)−C(14) 1.370(4); C(11)−C(12) 1.410(4); C(11)−C(16) 1.398(4); C(12)−C(13) 1.387(5); C(13)−C(14) 1.380(5); C(14)−C(15) 1.392(4); C(15)−C(16) 1.392(5); P(2)−Ru(1)−P(3) 157.50(3); C(5)−Ru(1)−C(6) 92.91(14).

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