Theory and Practice

Roald Hoffmann

One Saturday morning in 1989, I went into Cornell's chemistry library, as I'm wont to do on Saturdays. Near the entrance there is a rack for the new journals that have come in during the week. On Monday they're taken away to another place in the library, to lie there for a year until bound. The new-journal rack is a place to look at what's new. The hundred-odd journals stare me in the face as I enter the library. They make me feel guilty that I might have missed something important. Once you get in the habit of reading them, you can't stop. You are caught in the web of the new. If you are really addicted, you come each day as the journals are put out. When I was a beginner in science, and had less pulling at me, that's what I did. Now I just channel my obsession, coming in weekends to my pantheon of new molecules. The new journals are put out during the librarian's working week, ending Friday. They will be taken away Monday. The weekend is the reader's interval.

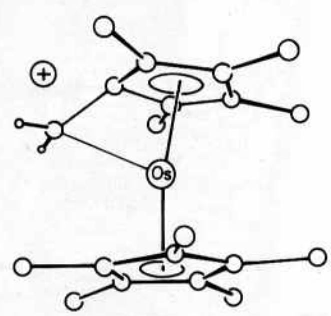
On that Saturday, I noticed an article in the *Journal of Organometallic Chemistry* by Margarita Rybinskaya from the Nesmeyanov Institute of Organoelement Chemistry in Moscow. She and her co-workers, mostly female (After I visited her laboratory, Rita said that she hoped I noticed that our obligatory tea was served by the most beautiful chemists in the world), are experts at making certain molecules: organometallics of iron, ruthenium and osmium, plus carbon and hydrogen. The novel molecule she reported synthesizing is structure 1, at right.

Note the osmium (Os) atom sandwiched between two rings—each made up of five carbon atoms and called a cyclopentadienyl—and the "extra" carbon at the top, which is distorted, leaning toward the osmium. That carbon is called a carbonium ion, and it lends a positive charge to the molecule as a whole. The compound is named colloquially the osmocenyl carbonium ion.

As I looked at Rybinskaya's paper, I thought of the corresponding dication (structure 2). In it, both rings bear an external carbonium ion—two positive charges on the molecule as a whole, therefore the dication label. I do not draw the expected bending of the carbonium ions toward the metal, just to make the overall geometry clearer.

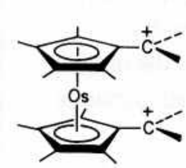
Roald Hoffmann is professor of chemistry at Cornell University. This essay will appear in Chemistry Imagined, *by Vivian Torrence and Roald Hoffmann, to be published by the Smithsonian Institution Press in the spring of 1993. Address: 222 Baker Laboratory, Cornell University, Ithaca, NY 14853–1301.*

Now there was nothing original in my thought. If someone paints one leg on a chair red, one is led to think of painting two or three or all four legs that color. And if you paint two legs, they can be opposite each other or adjacent. Much of science is like that. But in structure 2, there was a new problem—one of potential interest to a theoretician. The relative orientation of the two carbonium-ion centers may vary. In structure 2, the two "arms" are depicted on top of each other. (This is shown again in structure 3 in side view and as a schematic projection from the top). In structure 4, the arms are rotated 90 degrees apart. The rotation is around the vertical axis—the axis piercing the centers of the cyclopentadienyl rings and containing the metal atom. In structure 5, the arms are 180 degrees apart.



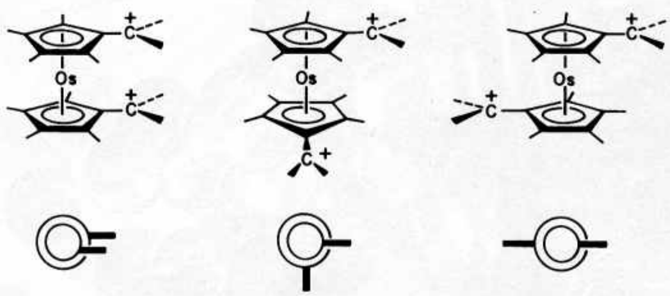
1

I sketched the disposition of the electrons on the osmium. I remember doing this in the library. The reasoning could be explained to a graduate student in inorganic chemistry in five minutes; if I do not reproduce it here, it is merely testimony to the fact that there is a reason why it takes five years to get a Ph.D. in chemistry. Anyway, in true back-of-the-envelope fashion, I came to the conclusion that the preferred geometry should have the external carbons rotated 45 degrees or 135 degrees relative to each other, as in structure 6 or structure 7.



2

I came back to my office and wrote a letter to Margarita. Now I would have written that letter even if I hadn't known her; communication is really easy in science. But, as it happens, I have known this outstanding Russian scientist for more than a decade. I remember well a snowy December day when I came in on the last plane they would let land in Sheremetovo for three days. Margarita and a driver met me and we drove for hours, past militia outposts, through deep, drifting snow—weather suitable for troikas, no one else crazy enough to be on the road.

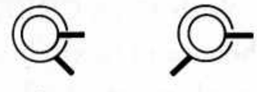


3 4 5

In the middle of the blizzard, Mother Russia and Grandfather Frost calling out to us, we skidded our way to a modern hostel. It was the last day of school in organometallic chemistry, and a homemade disco was under way, complete with a rotating, mirrored ball jury-rigged from lab supplies, American hard rock on the tape. A hundred organometallic chemists danced on their last night there, joining hands to sing a song by Bulat Okudzhava. While outside....

In my letter to Margarita, in English because I'm afraid of writing Russian even though I speak the language, I wrote something along the following lines: Fantastic that you've made the osmocenyl carbonium ion! Wouldn't it be interesting to make the dication? There are some predictions we could make about its structure.

Margarita replied, in a while. (Sad to say, it takes six weeks for a letter to go either way between the U.S. and the then U.S.S.R. Who is inefficient? Who reads them? I don't want to know.) She wrote, "Dear Roald," in English; but then, being afraid of how poor her English is, although she has to use it in her papers because, like it or not, broken English has become the international language of science—she continued in Russian. Great, we'll try, she said. Meanwhile do your calculations, maybe we can publish our work together.

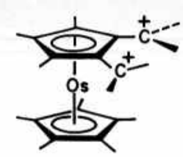


6 7

In my laboratory at the time was another Russian, Ruslan Minyaev, from Rostov-on-Don University. I had met Ruslan in 1985 in Rostov. We had visited the old Don Cossack communities together; we swam in the strong currents of the Don. I liked the way Ruslan did his science, and how he cared for drawings of chemical structures. So I invited him to Cornell. Because he wasn't a party member and was at a university, which is lower on the Russian totem pole than their Academy of Sciences, and because perestroika took its time to truly materialize, it was almost four years before he received permission to visit.

I asked Ruslan if he was interested in studying the cation that Margarita's laboratory was presumably working hard at making. I liked the idea of one Russian in Ithaca working theoretically on a molecule that another Russian in Moscow was synthesizing. And, Russia being a big country, Margarita and Ruslan didn't know each other at the time. I liked being a matchmaker.

In time, the numbers spewed out of our computer, telling us: No, the molecule did not want to be in geometry 6 or 7, as I had predicted. Insubordinate, it instead preferred structure 4: the two carbonium-ion centers rotated by 90 degrees relative to each other. What right had this computer to tell me the molecule would not be doing what I so cleverly thought it should be doing? Well, Ruslan eventually came up with an explanation, one simple enough to make me want to kick myself in the behind for not having seen it earlier.



8

In the midst of this theoretical contretemps, Margarita wrote: You'll be glad to learn that we've made the dication, just as you predicted. (She knows the way to a theoretician's heart!) I turned the page to her drawing and there was structure 8: Not the dication I had thought of, but rather another one with, sure enough, two carbonium ions in the molecule, but both on one ring instead of one each on the two separate rings!

Margarita had made an isomer of the molecule I wanted—a molecule that was the same, but not the same. In my earlier letter, I had violated a basic chemical principle: I failed to supplement my words with a chemical structure, a little drawing. There was no fault in what Margarita did. On the contrary, she had made a molecule no one had made before, a first! So while Ruslan scrambled to do theory on Margarita's molecule, so that we could write a joint paper on it, I had to tell her: Please, try to make the other one. She did try, but it's harder. They're still trying.

Bibliography

Kreidlin, A. Z., E. I. Fedin, P. V. Petrovskii, M. I. Rybinskaya, R. M. Minyaev and R. Hoffmann. 1991. Synthesis, NMR spectra, and molecular orbital calculations of Ruthenium and Osmium dications of the type $[C_5Me_5MC_5Me_3(CH_2)_2]^{2+}$. *Organometallics* 10:1206–1209.

Yanovsky, A. I., Yu. T. Struchkov, A. Z. Kreidlin and M. I. Rybinskaya. 1989. Crystal and molecular structure of the salt $[C_5Me_5RuC_5Me_4CH_2]^+BPh_4^- \bullet CH_2Cl_2$. *Journal of Organometallic Chemistry* 369:125–130.