



Communication

Redetermination of the O–O bond length in the dioxygen-adduct of Vaska's complex

Hélène Lebel*, Chehla Ladjel, Francine Bélanger-Gariépy, Frank Schaper

Département de chimie, Université de Montréal, 2900, Boul Edouard Montpetit, Montréal, Québec, Canada H3T 1J4

ARTICLE INFO

Article history:

Received 26 March 2008

Received in revised form 15 May 2008

Accepted 16 May 2008

Available online 24 May 2008

Keywords:

Iridium

Vaska's complex

O–O Bond length

Dioxygen complex

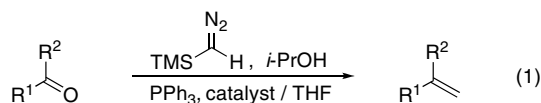
ABSTRACT

Solid state structural studies were performed with $(\text{Ph}_3\text{P})_2\text{IrCl}(\text{CO})(\text{O}_2)$ and the O–O length redetermined to be 1.47(1) Å in contrast to results reported earlier.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Transition metal-catalyzed methylenation reactions with trimethylsilyldiazomethane have been previously reported by us (Eq. (1)) [1]. As part of this work, we were interested in the mechanism of activation of trimethylsilyldiazomethane with metal complexes. We have hypothesized the formation of a *N*-coordinated intermediate, rather than a metal carbene with a ruthenium complex [2]. More recently we found that Vaska's complex was also capable of catalyzing the methylenation reaction with trimethylsilyldiazomethane [3].



catalyst: $\text{RhCl}(\text{PPh}_3)_3$ (2.5 mol%)
 $\text{RuCl}(\text{NO})(\text{PPh}_3)_2$ (5 mol%)
 NHCCuCl (5 mol%)
 $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (2.5 mol%)

To probe our mechanistic proposal, we then performed a number of crystallization experiments with trimethylsilyldiazomethane and iridium complexes, as these are known to lead to nitrogen-containing products with diazo compounds [4]. In the course of these solid state structural studies, a crystal structure of dioxygen-Vaska's complex $(\text{Ph}_3\text{P})_2\text{IrCl}(\text{CO})(\text{O}_2)$ was obtained

which featured a unprecedented O–O bond distance for this complex. This note describes the details of this study.

2. Results and discussion

2.1. Initial solid state structural studies

As part of our studies of reactions between iridium complexes and diazo compounds, we undertook an X-ray diffraction study of a crystal obtained from a mixture of Vaska's complex and trimethylsilyldiazomethane. The obtained structure was initially assigned as a nitrogen adduct of Vaska's complex, i.e., $(\text{Ph}_3\text{P})_2\text{IrCl}(\text{CO})(\text{N}_2)$, which was however in contradiction with the elemental analysis showing no nitrogen content and the coordination mode of the "N₂"-ligand. The crystal structure showed a trigonal bipyramidal coordination of the Ir with the supposed dinitrogen ligand in the equatorial plane, in a non-bridging η^2 -coordination. While this coordination mode is unprecedented for dinitrogen [5], it is very common for dioxygen [6]. Refinement of the structure as a dioxygen ligand yielded indeed better agreement factors and we identified (*vide infra*) the compound as the known dioxygen adduct $(\text{Ph}_3\text{P})_2\text{IrCl}(\text{CO})(\text{O}_2)$, **1** with an O–O bond length of 1.465(4) Å [7]. The molecular structure of **1** has been previously determined by an X-ray single crystal diffraction study at room temperature and reported in 1964 [8]. The authors reported an O–O bond length of 1.30 ± 0.03 Å, which is intermediate between that of O_2 (1.21 Å) and O_2^- anion (1.49 Å), but agrees well with that of O_2^- (1.33 Å). The dioxygen ligand should then be a superoxo with a formal oxidation state of II at the iridium center. However, iridium complex **1** was diamagnetic [8b] and showed an $\nu(\text{O}-\text{O})$ stretching frequency at 855 cm^{-1} [9], and the authors consequently assigned

* Corresponding author. Tel.: +1 514 343 5826.

E-mail address: helene.lebel@umontreal.ca (H. Lebel).

the ligand as a peroxo with reversible binding properties. Subsequently, there were some doubts about the value of 1.30 Å for the O–O bond length [10], as other closely related compounds showed values between ~1.4 and 1.5 Å [7]. To establish the correct value of the O–O bond length, we then decided to re-investigate in details the crystal structure of **1**.

2.2. Complex synthesis

Complex **1** was prepared from a reaction between Vaska's complex and oxygen in THF and was isolated as light orange, air-stable crystals. In the FT-IR spectrum, an $\nu(\text{O}-\text{O})$ stretching frequency was observed as a band of medium intensity at 856 cm^{-1} , in good agreement with values previously reported for this complex (855 cm^{-1} and 854 cm^{-1} , respectively) [9,11] and comparable to those observed for $(\text{Ph}_3\text{P})_2\text{Ir}(\text{O}_2)\text{I}(\text{CO})$ (862 cm^{-1}) [12] and $(\mu\text{-dppp})_2\{\text{IrCl}(\text{CO})\}_2(\text{O}_2)$ (843 cm^{-1}) [13]. The difference in the $\nu(\text{CO})$ stretching frequency between Vaska's complex and **1** is 47 cm^{-1} (1949 and 1996 cm^{-1} , respectively), in good agreement with the literature [14]. Finally, the ^{31}P NMR spectrum shows 2 equiv. PPh_3 ligands, which give rise to a singlet resonance at δ 5.34.

2.3. Crystal structure determinations

As described previously [8] **1** crystallized in the triclinic space group $P\bar{1}$. An X-ray diffraction study at 150 K showed a trigonal bipyramidal coordination of the iridium atom (Fig. 1). As observed for Vaska's complex [15] and in agreement with the previous study, the chloride and carbon monoxide ligands were found to be disordered [8]. The Ir–C–O bond angles of 173° and 174° are comparable to those observed in Vaska's complex (175°), where a similar CO/Cl disorder was observed. A comparison of selected

geometrical data between the previous study and ours is presented in Table 1.

The obtained geometrical data is identical between the two studies (in the limit of their accuracy), with the notable exception of the O3–Ir–O4 bond angle and the O3–O4 bond distance of $1.465(4)\text{ \AA}$, which is significantly longer than the $1.30 \pm 0.03\text{ \AA}$ reported previously. The longer bond distance found here agrees more closely with a description of the dioxygen ligand as O_2^{2-} , in agreement with the obtained IR data. The O–O distance of the closely related complex $(\text{EtPh}_2\text{P})_2\text{Ir}(\text{O}_2)\text{Cl}(\text{CO})$ was reported to be 1.469 \AA [16], also in good agreement with the value found here. An attempt to simulate the conditions of the earlier study (restriction to reflections with $\theta < 18^\circ$ and $I > 2\sigma(I)$, isotropic refinement) did not influence the O–O bond distance. While the better agreement with comparable compounds and spectroscopic results, as well as the higher amount and the better quality of the collected data, make us confident in the structural values determined, we were curious about the reasons for the mismatch with the older study, which seemed to be of sufficient quality.

We have considered several systematical errors in X-ray diffraction studies, which might cause a shortening of observed bond lengths, notably the effects of libration, disorder and decomposition. Libration effects have been reported previously to be responsible for artificially short O–O bond lengths [17]. Room temperature diffraction studies of **1**, however, both with Mo radiation (as used in the original study) and with Cu radiation, did not yield structural data different from our low temperature results (Table 1, entries 3 and 4). Insufficiently described disorder in a molecule was another explanation offered for incorrect O–O distances [18]. Although an influence of the Cl/CO disorder on the positioning of the dioxygen ligand in **1** is imaginable, careful inspection of the thermal displacement parameters obtained in the low temperature study tends to disprove this theory. Size and orientation of the thermal displacement parameters of the O3 and O4 atoms ($U_{\text{eq}} = 0.034$ and 0.044 \AA^2 , respectively) do not indicate any pronounced disorder of these atoms, when compared to the rest of the molecule (cf. $0.03\text{--}0.05\text{ \AA}^2$ for C_{Ph} , 0.02 \AA^2 for P). Nolte et al. found that decomposition of a single crystal of $[(\text{dppe})_2\text{Ir}(\text{O}_2)]\text{PF}_6$ caused an apparent change in the O–O bond length; in their case an elongation from 1.52 to 1.74 \AA [10]. While we did not conduct any decomposition studies, we reinvestigated the same crystal after several days of storage at ambient temperatures (entry 5). The data was of general lower quality, and the O–O bond length increased to 1.76 \AA . While decomposition has thus clearly an influence on the O–O bond length, it does not provide an explanation for the shortened bond length observed in the previous study. There is no indication that the longer bond length observed here might be due to crystal decomposition.

2.4. Conclusion

While the discrepancies between the two studies cannot be explained without access to the original crystals, the low temperature used in this study, the higher number and the better quality of the obtained reflection data, its improved agreement values and internal consistency, the identical data obtained from three independent crystals (not provided in Table 1) and the better agreement with literature data of comparable compounds, all argue that the data presented here is a better description of the structural reality. With the correction of the values for the O–O distance in **1** (1.30 \AA corrected to 1.47 \AA) and in $[(\text{dppe})_2\text{Ir}(\text{O}_2)]\text{PF}_6$ (1.74 \AA corrected to 1.52 \AA) [10], O–O distances in $\text{Ir}(\eta^2\text{-O}_2)$ complexes now range from 1.43 to 1.53 \AA (based on 12 structures with an accuracy better than $\pm 0.05\text{ \AA}$), which confirms the statement made by Vaska in 1976 that “coordinated O_2 shows, or at least

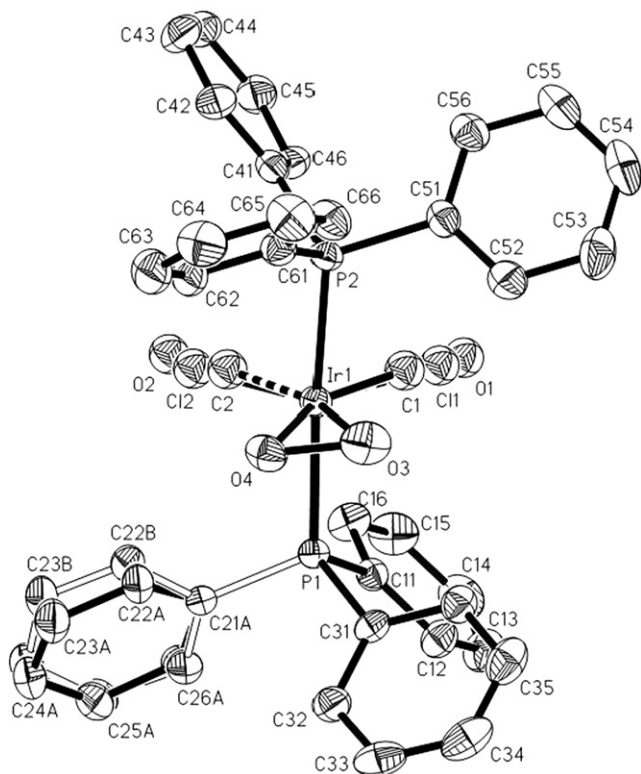


Fig. 1. Molecular structure of complex **1**. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

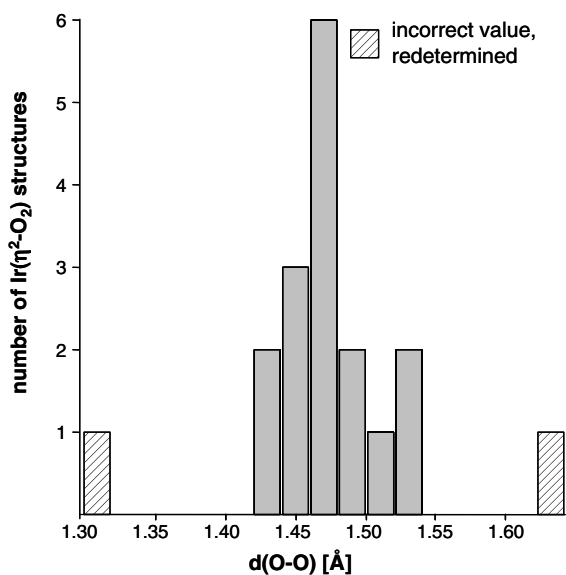
Table 1
Selected bond lengths [Å] and angles [°] for **1** at different temperatures and radiations

| | Original study (#1) ^a | Low T (#2) | Room temp. (#3) | Room temp. (#4) | Aged crystal (#5) |
|--------------------------------|----------------------------------|------------------|------------------|------------------|-------------------|
| Temperature (K) | 296 | 150 | 296 | 296 | 296 |
| Radiation | MoK α | CuK α | CuK α | MoK α | CuK α |
| R ₁ (observed data) | 7.1% | 3.1% | 4.1% | 4.0% | 9.9% |
| O3–O4 | 1.30(3) | 1.465(4) | 1.492(7) | 1.470(5) | 1.76(2) |
| Ir–O3 | 2.04(3) | 2.038(3) | 2.010(4) | 1.992(4) | 2.090(14) |
| Ir–O4 | 2.09(3) | 2.064(3) | 2.090(4) | 2.106(3) | 2.115(11) |
| O3–Ir–O4 | 36.7(9) | 41.9(1) | 42.6(2) | 41.9(1) | 49.4(7) |
| Ir–P1 | 2.36(1) | 2.359(1) | 2.370(1) | 2.379(1) | 2.378(4) |
| Ir–P2 | 2.38(1) | 2.363(1) | 2.373(1) | 2.379(1) | 2.379(4) |
| P1–Ir–P2 | 172.8(5) | 173.9(1) | 174.0(1) | 174.0(1) | 175.3(1) |
| P1–Ir–O3/4 | 84.1(9); 90.6(7) | 85.4(1); 90.1(1) | 85.1(1); 90.3(1) | 85.4(1); 90.1(1) | 85.5(3); 92.1(4) |
| P2–Ir–O3/4 | 85.4(7); 89.2(9) | 83.8(1); 90.7(1) | 83.9(1); 91.2(1) | 84.0(1); 91.0(1) | 83.2(4); 91.7(3) |
| Δ Ir–P ^b (Å) | 0.02 | 0.003 | 0.003 | 0.000 | 0.001 |
| Δ P–C ^c (Å) | | 0.014 | 0.024 | 0.012 | 0.048 |

^a Data taken from Ref. [8]. It should be noted that the O–O distance in Ref. [8] is reported as 1.30(3) Å as well as 1.30 ± 0.03 Å.

^b Δ Ir–P = |d(Ir–P1) – d(Ir–P2)|.

^c Δ P–C = d(P–C)_{max} – d(P–C)_{min}.

**Fig. 2.** O–O distances observed in several Ir(η²-O₂) compounds.

strongly tends to show, a constant state in either class of compounds" (Fig. 2) [7c].

3. Experimental

3.1. Synthesis of IrCl(O₂)(CO)(PPh₃)₂ **1**

Dioxygen was bubbled through a solution of (Ph₃P)₂IrCl(CO) (0.010 g, 0.028 mmol) in THF (5 mL) for 3 h at room temperature. The solvent was evaporated and the resulting powder dissolved in THF and crystallized by layering with hexane.

3.2. X-ray diffraction studies

Cell refinement and data reduction were done using APEX2 [19]. Structures were solved by direct methods using SHELXS97 and refined on F² by full-matrix least squares using SHELXL97 [20]. Non-hydrogen atoms were refined anisotropically. The disordered CO and Cl ligands were refined isotropic. U_{iso} was constrained to be identical for the disordered C1, C2, O1 and O2, and Cl1 and Cl2, respectively. Dataset #5 was of very low quality. Refinement was possible only using additional geometric restraints. Hydrogen

Table 2
Details of X-ray diffraction studies of **1**

| | Low T (#2) | Room temp. (#3) | Room temp. (#4) | Aged crystal (#5) |
|--|---|--------------------|----------------------|--------------------|
| Formula; M _w (g/mol); F(000) | C ₃₇ H ₃₀ ClIrO ₃ P ₂ ; 812.20; 800 | | | |
| Crystal color, form & Size (mm) | Pale yellow fragment; 0.04 × 0.07 × 0.12 | | | |
| Crystal system; space group; Z | Triclinic; P $\bar{1}$; 2 | | | |
| Wavelength; T (K) | 1.54178; 150 | 1.54178; 296 | 0.71073; 296 | 1.54178; 296 |
| D _{calc} (g/cm ³) | 1.655 | 1.612 | 1.615 | 1.612 |
| Unit cell | | | | |
| a (Å) | 9.7273(5) | 9.8066(8) | 9.802(2) | 9.8026(11) |
| b (Å) | 9.8689(5) | 9.9432(8) | 9.936(3) | 9.9196(9) |
| c (Å) | 17.0963(8) | 17.3223(14) | 17.319(4) | 17.4084(19) |
| α (°) | 95.763(3) | 96.477(4) | 96.653(4) | 97.018(5) |
| β (°) | 90.847(2) | 91.346(4) | 91.375(4) | 91.857(7) |
| γ (°) | 93.367(2) | 93.973(4) | 94.168(4) | 94.113(5) |
| V (Å ³) | 1629.74(14) | 1673.4(2) | 1670.1(7) | 1674.3(3) |
| θ Range (°); completeness | 2.6–72.0; 0.96 | 2.6–72.7; 0.97 | 1.2–31.4; 0.96 | 2.6–68.6; 0.86 |
| Reflections: collected/independent; R _{int} | 19594; 6120; 0.041 | 39900; 6433; 0.063 | 117094; 10581; 0.112 | 23802; 5237; 0.086 |
| μ (mm ⁻¹); abs. corr. | 9.898; multi-scan | 9.640; multi-scan | 4.208; multi-scan | 9.635; multi-scan |
| R ₁ (F); wR (F ²) [I > 2σ(I)] | 3.1%; 7.9% | 4.1%; 10.9% | 4.0%; 7.0% | 9.9%; 24.4% |
| R ₁ (F); wR (F ²) (all data) | 3.2%; 8.0% | 4.9%; 11.2% | 9.9%; 7.6% | 13.4%; 26.6% |
| Goodness-of-fit (F ²) | 1.046 | 1.071 | 0.925 | 1.096 |
| Residual electron density | 1.16 | 1.08 | 1.24 | 3.14 |

Instrumentation: #2, #4: Bruker Platform, SMART4K, rotating anode; #3: Bruker Smart, APEX2, sealed tube; #5: Bruker Microstar, Platinum 135, rotating anode.

atoms were refined isotropic on calculated positions using a riding model. Further experimental details are listed in Table 2.

Acknowledgments

This research was supported by NSERC (Canada), the Canadian Foundation for Innovation, the Canada Research Chair Program and the Université de Montréal. Acknowledgement is also made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research.

Appendix A. Supplementary material

Further details of the X-ray diffraction studies. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.05.025](https://doi.org/10.1016/j.jorganchem.2008.05.025).

References

- [1] (a) H. Lebel, V. Paquet, C. Proulx, *Angew. Chem., Int. Ed.* 40 (2001) 2887; (b) G.A. Grasa, Z. Moore, K.L. Martin, E.D. Stevens, S.P. Nolan, V. Paquet, H. Lebel, *J. Organomet. Chem.* 658 (2002) 126; (c) H. Lebel, V. Paquet, *Org. Lett.* 4 (2002) 1671; (d) H. Lebel, D. Guay, V. Paquet, K. Huard, *Org. Lett.* 6 (2004) 3047; (e) H. Lebel, V. Paquet, *J. Am. Chem. Soc.* 126 (2004) 320; (f) V. Paquet, H. Lebel, *Synthesis* (2005) 1901; (g) H. Lebel, M. Davi, S. Diez-Gonzalez, S.P. Nolan, *J. Org. Chem.* 72 (2007) 144; (h) H. Lebel, M. Parmentier, *Org. Lett.* 9 (2007) 3563.
- [2] H. Lebel, V. Paquet, *Organometallics* 23 (2004) 1187.
- [3] H. Lebel, C. Ladjel, *Organometallics* 27 (2008) 2676.
- [4] (a) See for instance: K.D. Schramm, J.A. Ibers, *J. Am. Chem. Soc.* 100 (1978) 2932; (b) K.D. Schramm, J.A. Ibers, *Inorg. Chem.* 19 (1980) 2435; (c) M. Cowie, S.J. Loeb, I.R. McKeer, *Organometallics* 5 (1986) 854; (d) Review: M. Dartiguenave, M.J. Menu, E. Deydier, Y. Dartiguenave, H. Siebald, *Coord. Chem. Rev.* 180 (1998) 623.
- [5] (a) B.A. MacKay, M.D. Fryzuk, *Chem. Rev.* 104 (2004) 385; (b) E.A. MacLachlan, M.D. Fryzuk, *Organometallics* 25 (2006) 1530.
- [6] M. Laing, M.J. Nolte, E. Singleton, *J. Chem. Soc., Chem. Commun.* (1975) 660.
- [7] (a) L. Vaska, J.W. DiLuzio, *J. Am. Chem. Soc.* 83 (1961) 2784; (b) L. Vaska, *Science* 140 (1963) 809; (c) L. Vaska, *Acc. Chem. Res.* 9 (1976) 175.
- [8] (a) J.A. Ibers, S.J. La Placa, *Science* 145 (1964) 920; (b) S.J. La Placa, J.A. Ibers, *J. Am. Chem. Soc.* 87 (1965) 2581.
- [9] C.A. Read, W.R. Roper, *J. Chem. Soc., Dalton Trans.* (1973) 1370.
- [10] M.J. Nolte, E. Singleton, M. Laing, *J. Am. Chem. Soc.* 97 (1975) 6396–6400.
- [11] J. Kovács, T. Decuir Todd, J.H. Reibenspies, F. Joö, D.J. Darensbourg, *Organometallics* 19 (2000) 3963.
- [12] J.A. McGinnety, R.J. Doedens, J.A. Ibers, *Inorg. Chem.* 6 (1967) 2243.
- [13] H.H. Wang, L.H. Pignolet, P.E. Reedy, M.M. Olmstead, A.L. Balch, *Inorg. Chem.* 26 (1987) 377.
- [14] L. Vaska, *Acc. Chem. Res.* 1 (1968) 335.
- [15] M.R. Churchill, J.C. Fettingner, L.A. Buttrey, M.D. Barkan, J.S. Thompson, *J. Organomet. Chem.* 340 (1988) 257.
- [16] M.S. Weininger, E.A.H. Griffith, C.T. Sears, E.L. Amma, *Inorg. Chim. Acta* 60 (1982) 67.
- [17] C.J. Cramer, W.B. Tolman, K.H. Theopold, A.L. Rheingold, *Proc. Natl. Acad. Sci.* 100 (2003) 3635.
- [18] (a) P. Comba, S. Kuwata, G. Linti, M. Tarnai, H. Wadeppohl, *Eur. J. Inorg. Chem.* (2007) 657; (b) S.K. Maiti, K.M. Abdul Malik, R. Bhattacharyya, *Inorg. Chem. Commun.* 7 (2004) 823; (c) S.K. Maiti, K.M.A. Malik, S. Gupta, S. Chakraborty, A.K. Ganguli, A.K. Mukherjee, R. Bhattacharyya, *Inorg. Chem.* 45 (2006) 9843; (d) K. Kanamori, K. Nishida, N. Miyata, T. Shimoyama, K. Hata, C. Mihara, K.i. Okamoto, Y. Abe, S. Hayakawa, S. Matsugo, *Inorg. Chem.* 43 (2004) 7127.
- [19] APEX2, Release 2.1-0; Bruker AXS Inc., Madison, USA, 2006.
- [20] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 64 (2008) 112.