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# Communications

## Unusual Tautomers in Dinuclear Metal Chemistry and Their Role in Oxidative-Addition Reactions of Chlorocarbons

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*Summary: The complex* [{Ir($\mu$-Pz)(CNBu$^t$)$_2$}$_2$(Cl)(CH$_2$Ph)] (**2**), *obtained by reaction of* [{Ir($\mu$-Pz)(CNBu$^t$)$_2$}$_2$] (**1**) *with* PhCH$_2$Cl, *presents a very unusual tautomeric equilibrium between the metal−metal-bonded and the mixed-valence complexes* [(CNBu$^t$)$_2$(Cl)Ir($\mu$-Pz)$_2$Ir(CH$_2$Ph)(CNBu$^t$)$_2$] *and* [(CNBu$^t$)$_2$Ir($\mu$-Pz)$_2$Ir(Cl)(CH$_2$Ph)(CNBu$^t$)$_2$], *respectively. This equilibrium allows the unprecedented oxidative-addition reaction of chloroalkanes such as* PhCH$_2$Cl *and* MeCO$_2$CH$_2$Cl *to the diiridium(II) complex* **2**, *resulting in the diiridium(III) complex* [{Ir($\mu$-Pz)(CH$_2$Ph)(CNBu$^t$)$_2$}$_2$($\mu$-Cl)]Cl *and the mixed-dialkyl complex* [(CNBu$^t$)$_2$(MeCO$_2$CH$_2$)Ir($\mu$-Pz)$_2$($\mu$-Cl)Ir(CH$_2$Ph)(CNBu$^t$)$_2$]Cl, *respectively.*

While tautomerism due to prototropic shifts is a well-established concept in organic[1] and organometallic chemistry,[2] tautomerism involving metal centers seems to be restricted to internal metal−ligand electron transfer (valence tautomers) in mononuclear complexes.[3] Dinuclear complexes are excellent candidates for new types of tautomeric equilibria that may provide pathways for some unusual reactions. In recent studies, we showed that the dinuclear complex [{Rh($\mu$-Pz)(CNBu$^t$)$_2$}$_2$] (Pz = pyrazolato) easily activates halocarbons,[4] including *gem*-di- and *gem*-trichloro derivatives. Herein, we report that reactions between [{Ir($\mu$-Pz)(CNBu$^t$)$_2$}$_2$] and monochloroalkanes occur within minutes at room temperature with Ir−Ir bond formation. It was found that there exists a tautomeric equilibrium involving one of the resulting diiridium(II) complexes, which allows a further unprecedented C−Cl oxidative addition. The reactions are clean and selective, with high yields (quantitative by NMR) being obtained in all cases.[5]

The reaction of [{Ir($\mu$-Pz)(CNBu$^t$)$_2$}$_2$] (**1**) with PhCH$_2$Cl in a 1:1 molar ratio results in the formation of orange crystals analyzing as [{Ir($\mu$-Pz)(CNBu$^t$)$_2$}$_2$(Cl)(CH$_2$Ph)] (**2**).

The X-ray structure of the metal−metal bonded complex [(CNBu$^t$)$_2$(Cl)Ir($\mu$-Pz)$_2$Ir(CH$_2$Ph)(CNBu$^t$)$_2$] (**2a**)

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[1] March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 4th ed.; Wiley-Interscience: New York, 1992; p 68.

[2] (a) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585. (b) Schlaf, M.; Lough, A. L.; Morris, R. H. *Organometallics* **1996**, *15*, 4423. (c) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596.

[3] (a) Roux, C.; Adams, D. M.; Itié, J. P.; Polian, A.; Hendrickson, D. N.; Verdaguer, M. *Inorg. Chem.* **1996**, *35*, 2846.

[4] (a) Tejel, C.; Ciriano, M. A.; Edwards, A. J.; Lahoz, F. J.; Oro, L. A. *Organometallics* **1997**, *16*, 45. (b) Tejel, C.; Ciriano, M. A.; Oro, L. A.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1994**, *13*, 4153.

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is shown in Figure 1.[6] The structure of **2a** shows the familiar boatlike conformation for the six-membered metallocycle "$Ir(N{-}N)_2Ir$" with a short intermetallic distance. The two added fragments are located at the exo sites, trans to the metal−metal bond. Complex **2a** represents the first fully characterized diiridium(II) complex resulting from a Cl−C oxidative addition. Mechanistic information pertaining to this reaction is provided by the addition of optically pure (−)-Methyl-(*S*)-2-chloropropionate to **1**, which similarly gives the two-center two-electron oxidative-addition product $[(CNBu^t)_2(Cl)Ir(\mu\text{-}Pz)_2Ir\{CH(Me)COOMe\}(CNBu^t)_2]$ (**3**). Solutions of **3** in benzene show static $^1H$ and $^{13}C\{^1H\}$ spectra corresponding to a single metal−metal-bonded species. Equimolecular amounts of the *R* and *S* configurations at the C atom were found using $Eu(hfc)_3$ (hfc = 3-(heptafluoropropylhydroxymethylene)-(+)-camphorato). The complete racemization observed in the formation of **3** suggests a free-radical mechanism for the formation of the Ir−Ir bond.

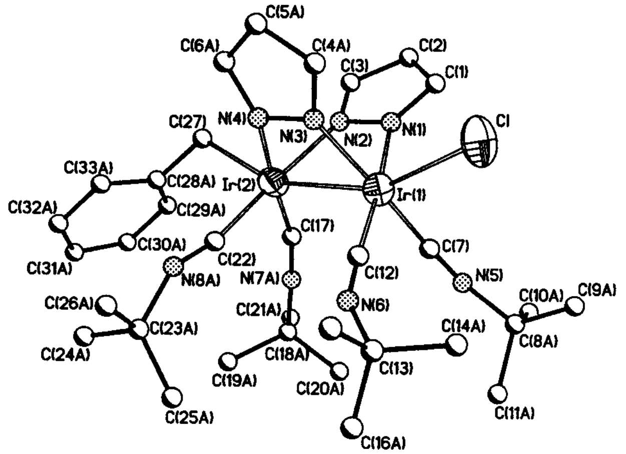

**Figure 1.** Molecular representation for the dinuclear complex $[(CNBu^t)_2(Cl)Ir(\mu\text{-}Pz)_2Ir(CH_2Ph)(CNBu^t)_2]$ (2a). Only one group of atoms has been drawn for disordered ligands. Selected bond lengths (Å) and angles (deg): Ir(1)−Ir(2) 2.7112(8), Ir(1)−Cl 2.532(3), Ir(1)−N(1) 2.092(7), Ir(1)−N(3) 2.066(8), Ir(1)−C(7) 1.848(10), Ir(1)−C(12) 1.874(10), Ir(2)−N(2) 2.074(8), Ir(2)−N(4) 2.059(9), Ir(2)−C(17) 1.909(11), Ir(2)−C(22) 1.940(13), Ir(2)−C(27) 2.195(8); Cl−Ir(1)−Ir(2) 155.14(8), Cl−Ir(1)−N(1) 90.9(2), Cl−Ir(1)−N(3) 91.5(2), Cl−Ir(1)−C(7) 93.6(3), Cl−Ir(1)−C(12) 94.0(3), N(1)−Ir(1)−N(3) 83.8(3), N(1)−Ir(1)−C(12) 175.0(4), N(3)−Ir(1)−C(7) 173.5(3), C(7)−Ir(1)−C(12) 88.7(5), C(27)−Ir(2)−Ir(1) 156.2(3), C(27)−Ir(2)−N(2) 91.8(3), C(27)−Ir(2)−N(4) 91.6(4), C(27)−Ir(2)−C(17) 92.3(4), C(27)−Ir(2)−C(22) 94.4(4), N(2)−Ir(2)−N(4) 85.6(3), N(2)−Ir(2)−C(22) 173.2(3), N(4)−Ir(1)−C(17) 176.0(4), C(17)−Ir(1)−C(22) 89.5(6).

Solutions of single crystals of **2** in benzene show two species in constant proportion which interconvert on the NMR time scale, as detected by negative cross-peaks in the NOESY spectrum. Moreover, a close inspection of the NOESY spectrum reveals that the major component (**2a**, 82%) is the species fully characterized by X-ray crystallography. Thus, an enhancement of the resonances for the $H^3$ pyrazolate protons on irradiation at the $CH_2$ group indicates their close proximity and the location of $CH_2Ph$ at the *exo* site for **2a**. The lack of NOE effects between $CH_2$ and the $H^3$ pyrazolate protons, along with the anomalous low-field shift of the former signal for the minor component (**2b**, 18%), suggests that the location of the $CH_2Ph$ group is at the endo site, as previously observed[4a] for the mixed-valence Rh(I)−Rh(III) complex $[(cod)Rh(\mu\text{-}Pz)_2Rh(I)(Me)(CNBu^t)_2]$. Thus, **2b** should be the *endo* conformer of the mixed-valence Ir(I)−Ir(III) complex $[(CNBu^t)_2Ir(\mu\text{-}Pz)_2Ir(Cl)(CH_2Ph)(CNBu^t)_2]$ (Scheme 1) related to **2a** by a metal-to-metal chlorotropic shift. A related chlorotropic shift has been previously described for the heterobimetallic complex $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Pz)_2Ir(Cl)(CO)_2]$.[7]

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(5) For analytical data of the new complexes see the Supporting Information. Selected spectroscopic data. **2**: IR (diethyl ether) $\nu = 2177$ (s, CN), 2133 (s, CN), 2091 (sh, CN), 2039 (m, CN) $cm^{-1}$; MS ($FAB^+$) *m/z* 977 ($M^+$, 100); $^1H$ NMR ($C_6D_6$, rt) **2a** $\delta$ 8.268 (d, 2.05 Hz, 2H, $H^3Pz$), 7.539 (d, 2.05 Hz, 2H, $H^5Pz$), 7.577 (d, 7.60 Hz, 2H, $H^{ortho}Ph$), 7.293 (t, 7.60 Hz, 2H, $H^{meta}Ph$), 7.052 (t, 7.60 Hz, 1H, $H^{para}Ph$), 5.989 (t, 2.05 Hz, 2H, $H^4Pz$), 4.146 (s, 2H, $CH_2$), 1.236 and 0.937 (s, 2 × 18H, $CNBu^t$); **2b** (from COSY spectrum) $\delta$ 8.478 (d, 2.16 Hz, 2H, $H^3Pz$), 8.194 (d, 2.16 Hz, 2H, $H^5Pz$), 7.210 (2H, $H^{ortho}Ph$), 7.052 (2H, $H^{meta}Ph$), 6.992 (1H, $H^{para}Ph$), 6.327 (t, 2.16 Hz, 2H, $H^4Pz$), 5.442 (s, 2H, $CH_2$), 1.036 and 0.876 (s, 2 × 18H, $CNBu^t$). **3**: IR (diethyl ether) $\nu$ 2181 (s, CN), 2139 (s, CN), 2080 (sh, CN), 2052 (m, CN) $cm^{-1}$; $^1H$ NMR ($C_6D_6$, rt) $\delta$ 8.218 (d, 2.04 Hz, 1H), 8.204 (d, 2.01 Hz, 1H), 8.080 (d, 1.68 Hz, 1H) and 7.688 (d, 1.84 Hz, 1H) $H^{3,3',5,5'}Pz$, 5.997 (t, 2.05 Hz, 1H) and 5.952 (t, 2.07 Hz, 1H, $H^{4,4'}Pz$), 4.047 (q, 6.79 Hz, 1H, $C\mathit{H}(CH_3)COOCH_3$), 3.692 (s, 3H, $CH(CH_3)COOC\mathit{H}_3$), 2.068 (d, 6.79 Hz, 3H, $CH(C\mathit{H}_3)COOCH_3$), 1.243, 1.239, 1.132 and 1.039 (s, 4 × 9H, $CNBu^t$); $^{13}C\{^1H\}$ NMR ($C_6D_6$, rt) $\delta$ 182.9 (CO), 136.6, 136.4, 134.3 and 134.1 ($C^{3,3',5,5'}Pz$), 138.7, 138.5, 123.6 (br) and 123.3 (br) (CN), 104.6 and 104.4 ($C^{4,4'}Pz$), 58.2 and 57.0 ($\mathit{C}\text{-}(CH_3)_3$), 49.6 ($CH(CH_3)COO\mathit{C}H_3$), 31.8, 31.0 and 30.8 ($C{-}(\mathit{C}H_3)_3$), 22.9 ($CH(\mathit{C}H_3)COOCH_3$), 7.0 ($\mathit{C}H(CH_3)COOCH_3$); MS ($FAB^+$) *m/z* 973 ($M^+$, 35), 937 ($M^+ - Cl$, 100). **4**: IR ($CH_2Cl_2$) $\nu$ 2220 (s, CN), 2187 (s, CN) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, rt) $\delta$ 7.644 (d, 2.28 Hz, 4H, $H^{3,5}Pz$), 7.228 (d, 7.20 Hz, 4H, $H^{ortho}Ph$), 7.143 (t, 7.20 Hz, 4H, $H^{meta}Ph$), 7.036 (t, 7.20 Hz, 2H, $H^{para}Ph$), 6.307 (t, 2.28 Hz, 2H, $H^4Pz$), 3.463 (s, 4H, $CH_2$), 1.077 (s, 36H, $CNBu^t$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt) $\delta$ 139.7 ($C^{3,5}Pz$), 149.8, 128.5, 128.4 and 125.0 (Ph), 106.8 ($C^4Pz$), 58.7 ($\mathit{C}{-}(CH_3)_3$), 29.9 ($C{-}(\mathit{C}H_3)_3$), 8.8 ($CH_2Ph$); MS ($FAB^+$) *m/z* 1069 ($M^+$, 100); $\Lambda_M$ (4.99 $10^{-4}$ M in acetone) 89 S $cm^2$ $mol^{-1}$. **5**: IR ($CH_2Cl_2$) $\nu$ 2224 (s, CN), 2193 (s, CN), 1713 (m, CO) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, rt) $\delta$ 7.689 (d, 2.22 Hz, 2H, $H^3Pz$), 7.621 (d, 2.22 Hz, 2H, $H^5Pz$), 7.189 (m, 4H, $H^{ortho,meta}Ph$), 7.092 (t, 6.82 Hz, 1H, $H^{para}Ph$), 6.262 (t, 2.22 Hz, 2H, $H^4Pz$), 3.641 (s, 3H, $COOCH_3$), 3.450 (s, 2H, $CH_2Ph$), 2.746 (s, 2H, $CH_2COOCH_3$), 1.444 (s, 18H, $CNBu^t$), 1.284 (s, 18H, $CNBu^t$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt) $\delta$ 180.4 (CO), 140.1 and 139.7 ($C^{3,\,5}Pz$), 149.8, 128.7, 128.4, and 125.3 (Ph), 106.9 ($C^4Pz$), 59.2 and 59.0 ($\mathit{C}\text{-}(CH_3)_3$), 50.9 ($COO\mathit{C}H_3$), 30.4 and 30.1 ($C{-}(\mathit{C}H_3)_3$), 8.8 ($CH_2Ph$), 1.6 ($\mathit{C}H_2COOCH_3$); MS ($FAB^+$) *m/z* 1050 ($M^+$, 100); $\Lambda_M$ (4.99 $10^{-4}$ M in acetone) 89 S $cm^2$ $mol^{-1}$.

(6) Crystal data for **2a**: $C_{33}H_{49}ClIr_2N_8{\cdot}0.3C_6H_6$, $M = 1001.08$, monoclinic, $P2_1/c$ (No. 14), $a = 21.862(6)$ Å, $b = 9.383(2)$ Å, $c = 23.552(7)$ Å, $\beta = 117.302(2)°$, $V = 4293(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.549$ g $cm^{-3}$, $F(000) = 1946$, $\lambda = 0.710\ 73$ Å, $T = 150.0(2)$ K, $\mu(MoK\alpha) = 6.286$ $mm^{-1}$. Data were collected on a Siemens P4 diffractometer by using an oil-coated rapidly cooled crystal of approximate dimensions 0.5 × 0.4 × 0.1 mm mounted directly from solution. Of a total of 8637 reflections collected by $\omega$ scans ($4° \leq 2\theta \leq 50°$), 7437 were unique. Data were corrected for absorption (Gaussian face-indexed method, SHELXTL v. 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI 1994); min and max transmission factors, 0.142 and 0.579, respectively. The structure was solved by direct methods (SIR92; Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined by full-matrix least-squares on $F^2$ (SHELXL-97; Sheldrick, G. M. Göttingen, 1997). After an isotropic refinement, it was evident the dinuclear molecule presented a heavy static disorder. This disorder affects not only the butylisocyanide groups but also benzyl and pyrazolate (one) ligands. The molecule disorder was carefully stepwise modeled after anisotropic refinement of all nondisordered atoms (fundamentally those directly bonded to the metals). In general, two different positions were included for each disordered moiety, which were refined with complementary occupancy factors, free displacement parameters, and, in some cases, some geometrical restrains (more details in Supporting Information). All disordered atoms were refined isotropically, and hydrogen atoms were only included in calculated positions for the nondisordered pyrazolate ligand. A disordered crystallization solvent molecule (benzene) was also detected and included in the last stages of the refinement. Final agreement factors were R1 0.0455 ($I \geq 2\sigma(I)$, 4494 reflections) and wR2 0.0676 (all data). Largest peak and hole in the final difference map 1.027 (close to Ir) and −0.892 e $A^{-3}$.

(7) Carmona, D.; Ferrer, J.; Mendoza, A.; Lahoz, F. J.; Reyes, J.; Oro, L. A. *Angew. Chem.* **1991**, *103*, 1192; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1171.

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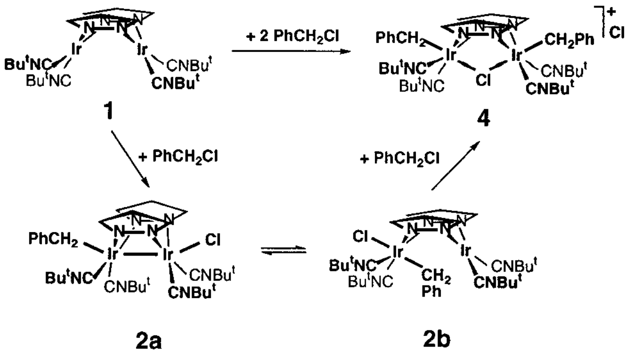
**Scheme 1**



Complexes **2a** and **2b** could be considered dinuclear valence tautomers or, alternatively, redox tautomers because they differ in the oxidation state of the metals.

Complex **2** reacts with $PhCH_2Cl$ to give the diiridium(III) complex $[\{Ir(\mu\text{-}Pz)(CH_2Ph)(CNBu^t)_2\}_2(\mu\text{-}Cl)]Cl$ (**4**) as a single isomer. The structure of **4**, shown in Scheme 1, places the $PhCH_2$ groups trans to the bridging chloride ligand, as deduced by NMR and NOE experiments. This protocol is also useful for the synthesis of mixed-dialkyl complexes such as $[(CNBu^t)_2(MeCO_2CH_2)Ir(\mu\text{-}Pz)_2(\mu\text{-}Cl)Ir(CH_2Ph)(CNBu^t)_2]Cl$ (**5**) by reaction of **2** with $MeCO_2CH_2Cl$ in benzene.

Known diiridium(II) complexes with halo derivatives are reluctant to undergo oxidative-addition reactions, and for this reason, the reaction **2** → **4** was unexpected. The only previously reported reaction involving dinuclear Ir(II) systems and halocarbyl moieties is the irreversible oxidative isomerization of complexes containing the "I−Ir−Ir−$CH_2I$" framework into methylene-bridged diiridium(III) compounds.[8] In this context, it is noteworthy that solutions of the diiridium(II) complex **3**, which is similar to **2a**, and $RCH_2Cl$ show no reaction after days. This suggests that the reactions of **2** reported herein occur because the tautomeric equilibrium provides an Ir(I) center in **2b**, which can undergo oxidative addition of a second molecule of $RCH_2Cl$. As the **2b** tautomer reacts, the equilibrium regenerates this active species and the reaction eventually goes to completion.

In conclusion, the existence of an equilibrium between dinuclear valence tautomers rationalizes the unprecedented activation of a C−Cl bond by diiridium (II) complexes.

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**Supporting Information Available:** Tables of elemental analyses for the new complexes and full experimental details of the structure determination, crystal data, atomic coordinates, thermal parameters, and bond distances and angles for **2a** and a molecular representation of this complex including the labeling system for all disordered atoms (10 pages). Ordering information is given on any current masthead page.

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[8] (a) Pinillos, M. T.; Elduque, A.; López, J. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1391. (b) Fernández, M. J.; Modrego, J.; Lahoz, F. J.; López, J. A.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1990**, 2587. (c) Brost, R. D.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 498.

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