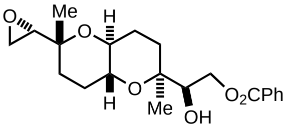
acetal **2**, $[\alpha]_D^{20} = -21.7$ ($c = 0.67$ in $CHCl_3$), was spectroscopically identical to that prepared previously[3] ($[\alpha]_D^{20} = -22.2$ ($c = 1.15$ in $CHCl_3$)[3]). The sense of asymmetric induction was the same as those observed in kinetic resolutions of terminal epoxides under similar reaction conditions. The enantiomeric excess of the desymmetrized product **14** was determined by chiral HPLC analysis of the corresponding benzoate **16**; comparison of **16** with a sample of low enantiomeric excess (prepared by mixing **16** with its enantiomer *ent*-**16**, also synthesized by desymmetrization of **3**) showed that the desymmetrized product **2** had >95% *ee.*



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The key step of our synthesis was the desymmetrization of a centrosymmetric molecule, an approach which had not previously been exploited in natural product synthesis. This strategy has, however, been applied in the desymmetrization of a 2-pyridone [4+4] photodimer,[10] the asymmetric reduction of a diketone,[11] and in the preparation of syndiotactic polymers.[12] The use of a desymmetrization, rather than a kinetic resolution strategy, enabled the product **2** to be obtained in high yield without compromising its enantiomeric excess. Our two-directional approach allowed the synthesis of the established intermediate **2** in eight steps and 34% overall yield. The key features of our synthesis of **2** include a) the use of no protecting groups, b) the use of only achiral reagents to control relative stereochemistry, and c) the use of a single chiral catalyst to induce asymmetry. The desymmetrization of centrosymmetric molecules, combined with a two-directional synthetic approach, is a powerful strategy which will find further application in the synthesis of natural products and biologically active compounds.

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Discrete Mixed-Valence Metal Chains: Iridium Pyridonate Blues**

Cristina Tejel, Miguel A. Ciriano,* B. Eva Villarroya, Raquel Gelpi, José A. López, Fernando J. Lahoz, and Luis A. Oro*

Discrete chains of metal atoms are of current interest from both theoretical and practical points of view. One synthetic approach to this type of compounds is based on ligand-assisted reactions using polydentate ligands, which is exemplified by several families of metal string complexes supported by oligo-α-pyridylamido ligands.[1] A second approximation involves the formation of metal–metal bonds between partially oxidized d^8 square-planar complexes, for which the platinum blues are the most representative examples.[2] Most of the reported platinum blues have been prepared from disymmetric square-planar dinuclear complexes with two amidate N-C-O-type ligands as bridges, and it has been claimed[2a–c] that the head-to-head (HH) configurations are essential to achieve the tetrametallic platinum chains. Moreover, it has been argued that the head-to-tail (HT) structures do not dimerize for steric reasons. In fact, all the reported structures of platinum blues are based on HH dimers. Other metals, for which square-planar complexes are common, such as rhodium, iridium, and gold, are suitable for forming such metallic chains, but few examples for these metals are known.[3] Herein we describe two new tetrametallic mixed-valence iridium compounds, which substantiate that dinuclear complexes with HT configurations are actually able to participate in metallic chains, while those with HH configurations generate the thermodynamically stable compounds.

An appropriate precursor for the formation of iridium pyridonate blues is the binuclear complex $[\{Ir(\mu\text{-}OPy)(CO)_2\}_2]$ (Opy = 2-pyridonate (**1**)). It was prepared, as purple microcrystals with metallic luster, by bubbling carbon monoxide through a solution of the complex $[\{Ir(\mu\text{-}OPy)(cod)\}_2]$ (cod = 1,5-cyclooctadiene) in toluene.[4] While the HT configuration of the α-pyridonate ligands was found in the solid state and in solution for the diolefinic complex, a bridging ligand rearrangement occurs on carbonylation. Thus, complex **1** was found to be a 1:1 mixture of the HH and the HT isomers in solution (Scheme 1). Noteworthy, these configurational isomers were found to be in a chemical equilibrium, as shown by the ^1H two-dimensional exchange (EXSY) spectrum.

Oxidation of a solution of **1** in toluene with diiodine (in a 2:1 molar ratio) at 50°C gives immediately an EPR-silent purple solution from which a crystalline blue solid (**2**) was isolated in excellent yield (95%) on addition of hexane.[5] This

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[*] Dr. M. A. Ciriano, Prof. L. A. Oro, Dr. C. Tejel, Dr. B. E. Villarroya, R. Gelpi, Dr. J. A. López, Dr. F. J. Lahoz
Departamento de Química Inorgánica
Instituto de Ciencia de Materiales de Aragón
Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza (Spain)
Fax: (+34) 976761143
E-mail: mciriano@posta.unizar.es
oro@posta.unizar.es

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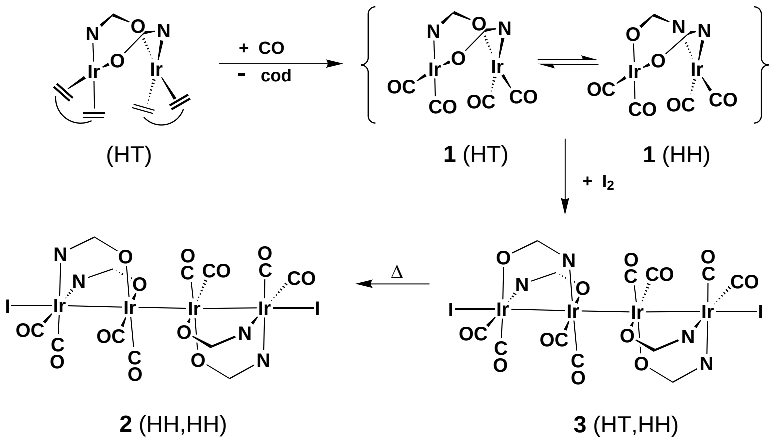

Scheme 1.

intensely colored solid was found to be the mixed-valence tetrametallic compound HH,HH-[{$Ir_2(\mu\text{-}OPy)_2(I)(CO)_4$}$_2$] (**2**), which is structurally and chemically similar to the platinum blues, with the metallic core Ir(1.50 +)$_4$. The X-ray crystal structure of **2** (Figure 1) showed two face-to-face dinuclear iridium complexes with a HH configuration joined together by an unsupported Ir–Ir bond between the *O,O*-coordinated Ir atoms.[6]

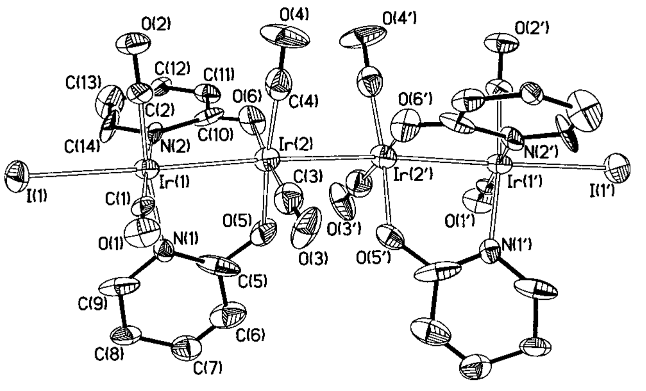

Figure 1. Molecular representation of the tetranuclear complex **2**. Primed atoms are related to the unprimed ones by the symmetry transformation $-x, y, -z+1/2$. Selected bond lengths [Å] and angles [°]: Ir(1)-Ir(2) 2.7015(15), Ir(2)-Ir(2') 2.750(2), Ir(1)-I(1) 2.843(2), Ir(1)-N(1) 2.14(2), Ir(1)-N(2) 2.113(19), Ir(1)-C(1) 1.86(2), Ir(1)-C(2) 1.85(3), Ir(2)-O(5) 2.007(18), Ir(2)-O(6) 2.035(17), Ir(2)-C(3) 1.84(3), Ir(2)-C(4) 1.91(3); Ir(2)-Ir(1)-I(1) 176.89(5).

The result of this reaction was more relevant when the reaction was carried out at temperatures below 0 °C. Under these conditions, green crystals of the novel compound HT,HH-[{$Ir_2(\mu\text{-}OPy)_2(I)(CO)_4$}$_2$] (**3**), containing a dimeric unit with the HT configuration, were obtained in 75 % yield by crystallization from methanol. The X-ray crystal structure of **3**,[7] (Figure 2) revealed the unsymmetrical tetrametallic chain formed by a linear stack of HT-[$Ir_2(\mu\text{-}OPy)_2(I)(CO)_4$] and HH-[$Ir_2(\mu\text{-}OPy)_2(I)(CO)_4$] units with an averaged oxidation state (1.50 +) for the iridium atoms of the chain.

In both complexes, the two dinuclear moieties, which are linked through an unsupported Ir–Ir bond, are arranged in an almost transoid conformation (mean torsion angles around the unsupported Ir–Ir bonds of 140(2)° in **2** and 142.3(8)° in **3**). All the Ir–Ir bond lengths within the metallic chains are similar, with those of the ligand-bridged metal–metal bonds (2.7015(15) Å in **2**, 2.6915(11) and 2.7114(11) Å in **3**) shorter than those of the central Ir–Ir bond (2.750(2) Å in **2**, 2.7793(11) Å in **3**). The three metal–metal bonds are nearly linear (168.20(6)° in **2**, 165.59(4)° and 168.17(4)° in **3**), and also the iodine atoms are linearly disposed with respect to these metal–metal bonds (176.89(5)° in **2**, 177.02(4)° and 168.83(5)° in **3**). This behavior has also been observed in the closely related pyrazolato-bridged complex [{$Ir_2(\mu\text{-}pz)_2(I)(CN\mathit{t}Bu)_4$}$_2$], although in this complex the intermetallic distances are slightly longer (2.7268(8) and 2.8037(10) Å), probably due to the different electronic properties of the ancillary ligands.[3e]

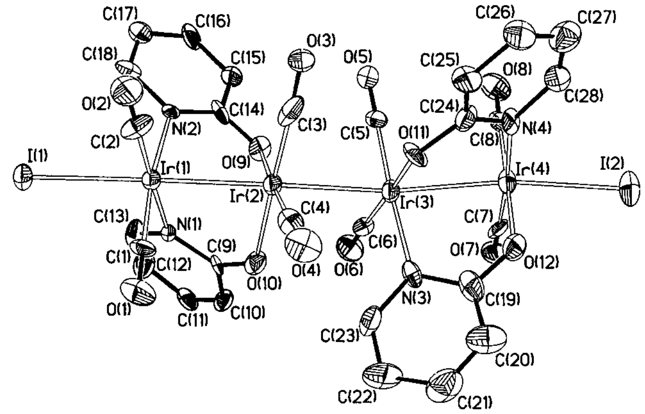

Figure 2. Molecular structure of the tetranuclear complex **3**. Selected bond lengths [Å] and angles [°]:Ir(1)-Ir(2) 2.6915(11), Ir(2)-Ir(3) 2.7793(11), Ir(3)-Ir(4) 2.7114(119), Ir(1)-I(1) 2.8470(15), Ir(4)-I(2) 2.8206(17), Ir(1)-N(1) 2.132(15), Ir(1)-N(2) 2.125(13), Ir(2)-O(9) 2.069(11), Ir(2)-O(10) 2.064(13), Ir(3)-N(3) 2.120(16), Ir(3)-O(11) 2.087(12), Ir(4)-N(4) 2.123(15), Ir(4)-O(12) 2.045(13), Ir-C(O) range 1.81(3)–1.885(18); Ir(2)-Ir(1)-I(1) 177.02(4), Ir(3)-Ir(4)-I(2) 168.83(5).

The stability found in solution for these diamagnetic tetrairidium chains is remarkable, and contrasts with most of the platinum blues, which disrupt upon dissolution.[2a] The iridium compounds reported here remain as such in solution, giving the expected resonances in the ^1H NMR spectra. Thus, complex **2** showed equivalent α-pyridonate groups, while **3** showed four nonequivalent α-pyridonate bridging ligands. On the other hand, a solution of the green complex **3** (HT,HH) was found to evolve into the blue isomer **2** (HH,HH) on heating at 60 °C in less than five minutes. This transformation, quantitative by ^1H NMR spectroscopy, occurred also at room temperature, but slowly. Indeed, the isomerization process was avoided when the preparation and isolation of **3** was carried out at low temperature. From these experiments, it is now clear that complex **2** is the thermodynamic isomer, while complex **3** corresponds to the kinetic isomer.

As commented above, the metal–metal distances and bond angles were similar for the isomers **2** and **3**, and no relevant steric strain arises from the participation of the HT configuration in the formation of the unsupported metal–metal bond. Furthermore, the steric bulk of the pyridonate rings does not hinder the formation the unsupported metal–metal bond. Therefore, one could envisage the accessibility of a hypothetical tetrametallic chain made of two HT units.

With the experimental confirmation of the intervention of HT dimers in tetrametallic chains, it seems likely that the lack of HT-pyridonate dimers in the platinum blues complexes should be attributed mainly to thermodynamic reasons rather than to steric factors.

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[5] Selected analytical and spectroscopic data for the new complexes: Complex **1**: elemental analysis (%) calcd for $C_{14}H_8N_2O_6Ir_2$: C 24.56, H 1.18, N 4.09; found: C 24.95, H 1.47, N 4.18; IR (toluene): $\tilde{\nu} = \nu(CO) =$ 2079 (s), 2048 (m), 2002 (s) cm^{-1}; ^{1}H NMR (C_6D_6, 333 K): HH isomer: $\delta = 7.64$ (d, $J = 6.9$ Hz, 2H), 6.60 (ddd, $J = 8.7, 6.9, 1.8$ Hz, 2H), 6.36 (d, $J = 8.7$ Hz, 2H), 5.77 (t, $J = 6.9$ Hz, 2H); HT isomer $\delta = 7.53$ (d, $J =$ 6.9 Hz, 2H), 6.60 (ddd, $J = 8.7, 6.9, 1.8$ Hz, 2H), 6.31 (d, $J = 8.7$ Hz, 2H), 5.77 (t, $J = 6.9$ Hz, 2H). Complex **2**: elemental analysis (%) calcd for $C_{28}H_{16}N_4O_{12}Ir_4I_2$: C 20.72, H 0.99, N 3.45; found: C 20.94, H 1.18, N 3.25; IR (toluene): $\tilde{\nu} = \nu(CO) = 2110$ (w), 2093 (s), 2066 (m), 2052 (s), 2027 (w) cm^{-1}; ^{1}H NMR (C_6D_6, 295 K): $\delta = 9.52$ (dd, 4H), 6.47 (ddd, 4H), 6.26 (dd, 4H), 5.73 (td); ^{13}C{^{1}H} NMR (C_6D_6, 295 K): $\delta = 175.3$, 167.2 (CO), 165.5 (CO), 152.7, 139.8, 116.7, 115.7. Complex **3**: elemental analysis (%) calcd for $C_{28}H_{16}N_4O_{12}Ir_4I_2$: C 20.72, H 0.99, N 3.45; found: C 20.52, H 0.78, N 3.44; IR (nujol): $\tilde{\nu} = \nu(CO) = 2087$ (s), 2071 (m) 2050 (sh), 2041 (s) 2006 (m) cm^{-1}; ^{1}H NMR: $\delta = 9.65$ (dd, 1H), 9.52 (dd (1H), 9.48 (dd, 1H), 9.21 (dd, 1H), 6.56 (m, 2H), 6.53 (m (1H), 6.45 (m, 1H), 6.38 (dd, 1H), 6.33 (dd, 1H), 6.20 (dd, 1H), 6.10 (dd, 1H), 5.90 (td, 1H), 5.86 (td, 1H), 5.74 (m, 2H).

[6] a) Crystallographically imposed twofold symmetry was observed relating the two halves of the tetranuclear complex. Crystal data for **2**: $C_{28}H_{16}I_2Ir_4N_4O_{12}$, $M_r = 1623.04$, laminar crystal ($0.14 \times 0.11 \times 0.06$ mm), monoclinic, space group $C2/c$, $a = 27.709(3)$, $b = 9.2163(10)$, $c = 16.9592(17)$ Å, $\beta = 124.274(2)^\circ$, $V = 3578.9(6)$ Å^{-3}, $Z = 4$, $\rho_{calcd} = 3.012$ g cm^{-3}, $F(000) = 2888$, $T = 150(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 16.615$ mm^{-1}). Data collected with a Bruker SMART APEX CCD diffractometer. Of 5545 measured reflections (2θ: 5–50°, ω scans 0.3°), 2662 were unique ($R_{int} = 0.0808$); a multiscan absorption correction was applied (PLATON program) with min./max. transmission factors of 0.204/0.436. Structure solved by Patterson and difference-Fourier maps; refined using SHELXTL. Final agreement factors were $R1 = 0.0808$ (1965 observed reflections, $F^2 > 4\sigma(F^2)$) and $wR2 = 0.2264$; data/restrains/parameters 2662/72/227; GOF = 1.039. Largest peak and hole in the final difference map 6.084 and -3.483 e Å^{-3}. The limited quality of the structural data (also the merging and agreement factors, and the high residuals) should be necessarily associated to the diffracting weakness, to the anisotropic morphology, and to the high absorption of the crystals. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165456 (**2**) and CCDC-165457 (**3**$\cdot 2\,CH_4O$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] Crystal data for **3**$\cdot 2\,CH_4O$: $C_{28}H_{16}I_2Ir_4N_4O_{12} \cdot 2\,CH_4O$, $M_r = 1687.13$, triclinic, space group $P\bar{1}$, $a = 10.2440(8)$, $b = 13.4751(10)$, $c = 15.2437$ (11) Å, $\alpha = 75.8696(15)$, $\beta = 71.2963(13)$, $\gamma = 78.1790(15)^\circ$, $V =$ 1914.4(2) Å^{-3}, $Z = 2$, $\rho_{calcd} = 2.927$ g cm^{-3}, $F(000) = 1516$, $T = 150(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 15.541$ mm^{-1}). Data collected as described for **3** with an elongated block ($0.20 \times 0.06 \times 0.04$ mm). Of 10303 measured reflections (2θ: 5–50°, ω scans 0.3°), 6555 were unique; a multiscan absorption correction was performed (SADABS program) with min./max. transmission factors of 0.119/0.583. Structure solution and refinement as described for **2**. Final agreement factors were $R1 = 0.0656$ (4735 observed reflections) and $wR2 = 0.1606$. Data/restrains/parameters 6555/61/487; GOF = 1.049. Largest peak and hole in the final difference map 3.638 and -2.464 e Å^{-3}.[6b]

Enantiomeric Discrimination in a Reiterative Domino Coupling Process: Cu^I-mediated *Syn* Cyclotrimerization of Racemic Polycyclic Trimethylstannyl Bromonorbornadienes**

Sergio Cossu,* Chiara Cimenti, Paola Peluso,
Antonio Paulon, and Ottorino De Lucchi

The fundamental concept of molecular discrimination considers the ability of a chemical object to identify, in the presence of alternative possibilities, a defined chemical counterpart through specific interactions.[1] When discrimination depends on the chiral properties of the chemical partners, only one of the events that derive from the possible stereochemical combinations can be realized.[1] In this context, a peculiar discrimination was observed during the self-coupling of racemic ketones that possess the bicyclo[2.2.1]heptene skeleton, either by means of aldol reactions or via organocuprate derivatives. The main feature of the reported

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[*] Dr. S. Cossu, Dr. C. Cimenti, Dr. P. Peluso, Dr. A. Paulon,
Prof. Dr. O. De Lucchi
Dipartimento di Chimica, Università Ca' Foscari di Venezia
Dorsoduro 2137, 30123 Venezia (Italy)
Fax: (+39) 041-257-8517
E-mail: cossu@unive.it

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