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New Cationic and Neutral Ru(II)- and Os(II)-dmso carbonyl Compounds

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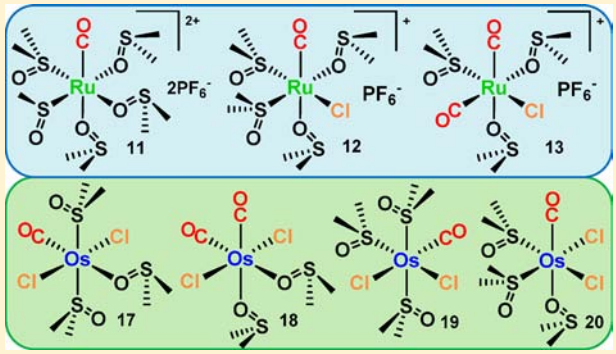
Supporting Information

ABSTRACT: The preparation and structural characterization of three cationic Ru(II)-dmso carbonyls and of four neutral mono- and dicarbonyl Os(II)-dmso derivatives is reported. The two monocarbonyl species *fac*-[Ru(CO)(dmso-O)$_3$(dmso-S)$_2$][PF$_6$]$_2$ (**11**) and *cis,cis,cis*-[RuCl(CO)(dmso-O)$_2$(dmso-S)$_2$][PF$_6$] (**12**) were obtained from the neutral monocarbonyl precursor *cis,trans,cis*-[RuCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**3**) upon stepwise replacement of the chlorides with dmso, that binds in each case through the oxygen atom. The dicarbonyl cationic complex *cis,cis,trans*-[Ru(CO)$_2$(dmso-O)$_2$(dmso-S)Cl][PF$_6$] (**13**) was instead obtained upon treatment of the neutral tricarbonyl precursor *fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (**8**) with AgPF$_6$ in the presence of DMSO: replacement of a Cl$^-$ with a dmso-O implied also the substitution of one CO ligand by another dmso (that binds through S *trans* to Cl). The Os(II) carbonyls *trans,trans,trans*-[OsCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**17**), *trans,cis,cis*-[OsCl$_2$(CO)$_2$(dmso-O)$_2$] (**18**), *cis,mer*-[OsCl$_2$(CO)(dmso-S)$_3$] (**19**), and *cis,trans,cis*-[OsCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**20**) were obtained by treatment of the Os(II)-dmso precursors *trans*-[OsCl$_2$(dmso-S)$_4$] (**14**) and *cis,fac*-[OsCl$_2$(dmso-O)(dmso-S)$_3$] (**15**) with CO. Each one of them is structurally similar to an already known Ru(II) analog, even though—in agreement with the expected greater inertness of Os(II)—more forcing reaction conditions were required for their preparation. Interestingly, compound **20** could not be isolated in pure form, but only as a 1:1 cocrystallized mixture with its precursor **15**. The dmso ligand is always bound through the oxygen atom when trans to CO. We are confident that the new Ru(II)- and Os(II)-dmso carbonyl species described here represent a contribution to expand the pool of complexes bearing some easily replaceable dmso ligands to be used as well-behaved precursors in inorganic synthesis.



INTRODUCTION

In the past we have thoroughly investigated the reactivity of the two isomeric Ru(II)-dmso chlorido precursors *cis,fac*-[RuCl$_2$(dmso-O)(dmso-S)$_3$] (**1**) and *trans*-[RuCl$_2$(dmso-S)$_4$] (**2**) toward carbon monoxide.[1,2] We found that, depending on the conditions, CO can replace from one to three dmso ligands, leaving the geometry of the two chlorides unchanged. We also observed that coordination of CO always induced the selective S-to-O linkage isomerization of the dmso trans to it. Several neutral species, often stereoisomers, were isolated and characterized and the reaction conditions for obtaining them in pure form were established. Namely: from **1** three monocarbonyl (*cis,trans,cis*-[RuCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**3**), *cis,cis,cis*-[RuCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**4**) and *mer*-[RuCl$_2$(CO)(dmso-S)$_3$] (**5**)), two dicarbonyl (*cis,cis,cis*-[RuCl$_2$(CO)$_2$(dmso-O)(dmso-S)] (**6**) and *cis,cis,trans*-[RuCl$_2$(CO)$_2$(dmso-S)$_2$] (**7**)), and one tricarbonyl species (*fac*-[RuCl$_2$(CO)$_3$(dmso-O)] (**8**)) were prepared, whereas from the *trans* isomer **2** one monocarbonyl (*trans,trans,trans*-[RuCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**9**)) and one dicarbonyl species (*trans,cis,cis*-[RuCl$_2$(CO)$_2$(dmso-O)$_2$] (**10**)) were obtained (Scheme 1). In addition, the unprecedented double bridged Ru(II) dimer [{*cis*-RuCl$_2$(CO)(dmso-S)}(μ-Cl)(μ-dmso-O,S){*cis*-RuCl(CO)(dmso-S)$_2$}], that features a rare example of bridging dmso-O,S ligand, was also obtained by refluxing the monocarbonyl complex **3** in acetone.[3]

We also found that these Ru(II) carbonyl compounds can be exploited as useful precursors in inorganic synthesis, as typically the dmso-O ligand trans to a carbonyl is selectively replaced by a neutral σ-donor N ligand (e.g., NH$_3$ or pyridine) under mild conditions.[1,4] Conversely, the dmso-S ligands − when present − require more forcing conditions for being replaced, and the CO and Cl ligands are not replaced at all by neutral monodentate ligands. Thus compounds **3**−**10** proved to be excellent alternatives in inorganic synthesis to the widely used, but in our opinion less versatile, precursors of Ru(II)-carbonyls: the dinuclear [RuCl$_2$(CO)$_3$]$_2$ species,[5] and the [Ru(CO)$_2$Cl$_2$]$_n$ polymer.[6] In particular, we extensively used compound **10** as selective precursor of the 90°-angular linker fragment *trans,cis*-{RuCl$_2$(CO)$_2$} for the construction of neutral porphyrin metallacycles.[7]

Given these premises, we reasoned that silver abstraction of one or both chlorides from the neutral species **3** − **10** in the

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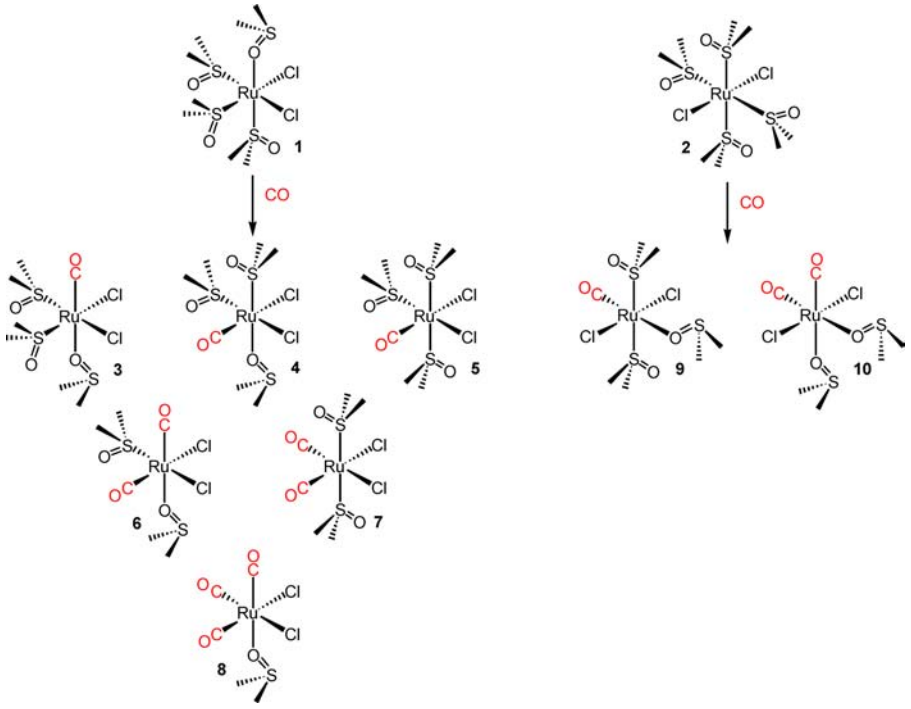
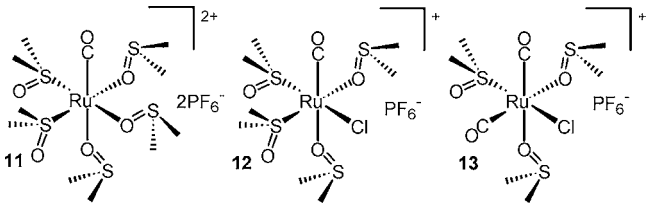
Scheme 1. Neutral Ru(II)-dmso carbonyl Complexes Obtained from *cis,fac*-[$RuCl_2$(dmso-O)(dmso-S)$_3$] (1) (left) and *trans*-[$RuCl_2$(dmso-S)$_4$] (2) (right) under Different Reaction Conditions



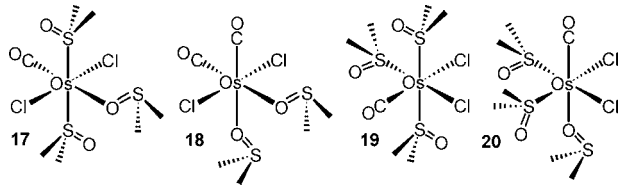
presence of DMSO might afford novel cationic Ru(II)-carbonyl compounds bearing some weakly bound dmso ligands. Such species might be expected to behave as selective precursors of geometrically well-defined octahedral cationic Ru(II)-CO fragments to be employed as linkers in the construction of supramolecular 2D and 3D architectures. For the moment we report here the results of our investigation on two easily accessible neutral compounds, the monocarbonyl **3** and the tricarbonyl **8**, that yielded the new mono- and dicarbonyl cationic complexes *fac*-[Ru(CO)(dmso-O)$_3$(dmso-S)$_2$][PF_6]$_2$ (**11**), *cis,cis,cis*-[RuCl(CO)(dmso-O)$_2$(dmso-S)$_2$][PF_6] (**12**) and *cis,cis,trans*-[Ru(CO)$_2$(dmso-O)$_2$(dmso-S)Cl][PF_6] (**13**) (Chart 1).

Chart 1



In addition, we also started to investigate the yet unexplored reactivity of the neutral Os(II)-dmso chlorido compounds *cis*- and *trans*-[$OsCl_2$(dmso)$_4$] toward carbon monoxide. In the past, we and others had demonstrated that even though Os(II) makes dmso complexes very similar to those of Ru(II), it has nevertheless a greater propensity, for electronic reasons, to bind dmso through S.[8−10] In fact, in addition to *trans*-[$OsCl_2$(dmso-S)$_4$] (**14**) − the kinetic product of the reduction of the Os(IV) precursor $OsCl_6^{2-}$ in DMSO and counterpart of **2** − two *cis* dichlorido complexes have been isolated and structurally characterized: *cis,fac*-[$OsCl_2$(dmso-O)(dmso-S)$_3$] (**15**)[10] − corresponding to **1** − and the all-sulfur linkage isomer *cis*-[$OsCl_2$(dmso-S)$_4$] (**16**),[9] whose counterpart is unknown in Ru(II)-dmso chemistry. Complex **16** was also proved to be the thermodynamically most stable isomer in solution.[10] We describe here four new neutral Os(II)-dmso carbonyls, each of them structurally similar to a Ru(II) counterpart: *trans,trans,trans*-[$OsCl_2$(CO)(dmso-O)(dmso-S)$_2$] (**17**), *trans,cis,cis*-[$OsCl_2$(CO)$_2$(dmso-O)$_2$] (**18**), *cis,mer*-[$OsCl_2$(CO)(dmso-S)$_3$] (**19**), and *cis,trans,cis*-[$OsCl_2$(CO)(dmso-O)(dmso-S)$_2$] (**20**) (Chart 2).

Chart 2



Interestingly, compound **20** could not be isolated in pure form, but only as a 1:1 cocrystallized mixture (**21**) with its precursor **15**.

EXPERIMENTAL SECTION

Materials. The precursors *cis,fac*-[$RuCl_2$(dmso-O)(dmso-S)$_3$] (**1**),[11] *cis,trans,cis*-[$RuCl_2$(CO)(dmso-O)(dmso-S)$_2$] (**3**),[1] *fac*-[$RuCl_2$(CO)$_3$(dmso-O)] (**8**),[1] *trans*-[$OsCl_2$(dmso-S)$_4$] (**14**),[8] and *cis,fac*-[$OsCl_2$(dmso-O)(dmso-S)$_3$] (**15**)[8] were prepared as described in the literature. An alternative procedure for the tricarbonyl complex **8** is described below. *fac*-[Ru(dmso-O)$_3$(dmso-S)$_3$][PF_6]$_2$ was prepared with a procedure similar to that reported by us for *fac*-[RuCl(dmso-O)$_2$(dmso-S)$_3$][PF_6],[12] using 2 equiv. of $AgPF_6$ instead of 1. $AgPF_6$ and other reagents were purchased from Sigma-Aldrich.

Instrumental Methods. Mono- (^{1}H (400 or 500 MHz), ^{13}C (100.5 MHz)) and bidimensional (^{1}H−^{13}C HSQC) NMR spectra

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were recorded on a JEOL Eclipse 400FT or on a Varian 500 spectrometer. All spectra were run at room temperature (r.t.); ^{1}H chemical shifts in D_2O were referenced to the internal standard 2,2-dimethyl-2,2-silapentane-5-sulfonate (DSS) at δ = 0.00. ^{1}H and ^{13}C chemical shifts in other solvents were referenced to the peaks of residual nondeuterated solvent (δ = 7.26 and 77.16 for $CDCl_3$, δ = 2.05 and 29.84 for $(CD_3)_2CO$). Solid-state infrared spectra (KBr) were obtained on a Perkin-Elmer 983G spectrometer. Peak intensities are given as broad (b), very strong (vs), strong (s), medium (m), and weak (w). Electrospray ionization mass spectra (ESI-MS), recorded on a Merck Hitachi M-8000 spectrometer in the positive ion mode using methanol as the solvent, gave no satisfactorily results and are not reported here. Since the nature of each complex was unambiguously established through the other techniques, no additional mass-spec experiment was attempted. Elemental analysis was performed at the Dipartimento di Chimica, Fisica e Ambiente, University of Udine (Italy). The acetone used in the preparations was previously dried over activated molecular sieves (3 Å).

Synthesis of the Complexes. Throughout the paper the ligands in the formulas are listed in alphabetical order, unless when this order is in conflict with a more rational use of the geometrical descriptors (e.g., in the case of **13**). Being this an explorative investigation, the isolated yields of the products were not optimized, and thus in some instances they are only moderate (or low, in the case of **13**). In addition, these compounds have a general tendency to give oils when treated with unsolubilizing solvents such as ethanol or diethyl ether (in which, nevertheless, they are slightly soluble even when ionic) or, at best, to crystallize very slowly (days) when the right mixture of solvents is found.

*fac-[RuCl$_2$(CO)$_3$(dmso-O)] (**8**).* The synthetic procedure originally described by us for the preparation of *fac*-[$RuCl_2(CO)_3$(dmso-O)] (**8**) requires refluxing *cis,fac*-[$RuCl_2$(dmso-O)(dmso-S)$_3$] (**1**) in ethanol under a stream of CO for 3h.[1] In the accomplishment of this work, we found an alternative synthesis for **8** that involves less consumption of CO: a 436 mg amount of **1** (0.9 mmol), suspended in 30 mL of ethanol, was treated in a pressurized vessel with CO (30 atm) at 80 °C for 4h. The resulting pale yellow solution was rotary evaporated completely, yielding 260 mg of a white solid that, according to ^{1}H NMR analysis, is a mixture of **8** (ca. 70%) and of the two known dicarbonyl complexes, *cis,cis,cis*-[$RuCl_2(CO)_2$(dmso-O)(dmso-S)] (**6**) and *cis,cis,trans*-[$RuCl_2(CO)_2$(dmso-S)$_2$] (**7**). Washing this solid with diethyl ether led to the partial extraction of **6** and **7**, but the purity of **8** was still unsatisfactory. Increasing the reaction time (up to 8h), CO pressure (up to 40 atm) and temperature (up to 100 °C) did not lead to a significant improvement in the yield of **8**, suggesting that the obtained mixture of products is the result of an equilibrium between the entering CO and the released dmso. We found, however, that when it was treated for a second run in the autoclave under the same conditions as above, pure **8** was obtained in a satisfactorily global yield of 80%.

*fac-[Ru(CO)(dmso-O)$_3$(dmso-S)$_2$][PF$_6$]$_2$ (**11**).* To a 80 mg amount of *cis,trans,cis*-[$RuCl_2$(CO)(dmso-O)(dmso-S)$_2$] (**3**) (0.18 mmol) dissolved in acetone (10 mL), DMSO (65.4 μL, 0.92 mmol, 5 equiv) and an excess of $AgPF_6$ (116.3 mg, 0.46 mmol, 2.5 equiv) were added and the mixture was refluxed for 4 h in the dark. After cooling, the mixture was filtered over Celite to remove AgCl and the filter was extensively washed with acetone. The colorless solution was rotary-evaporated to an oil. Addition of ethanol (5 mL) afforded the product as a white solid that was filtered, washed with ethanol and diethyl ether and vacuum-dried. Yield 100 mg (67%). Elemental analysis calcd for [$C_{11}H_{30}F_{12}O_6P_2RuS_5$] ($M_w$: 809.64): C 16.3; H 3.73. Found: C 16.4; H 3.68. The complex is soluble in DMSO, CH_3COCH_3 and CH_3NO_2, partially soluble in CH_3OH and H_2O, and insoluble in CH_3CH_2OH, $CHCl_3$ and CH_2Cl_2. Crystals suitable for X-ray analysis were obtained by slow dropwise addition of diethyl ether into an acetone solution of the complex. ^{1}H NMR (D_2O, δ ppm): 3.45 (s, 6H, CH_3 dmso-S), 3.38 (s, 6H, CH_3 dmso-S), 3.05 (s, 6H, CH_3 dmso-O), 3.03 (s, 6H, CH_3 dmso-O) 3.01 (s, 6H, CH_3 dmso-O). ($(CD_3)_2CO$, δ ppm): 3.54 (s, 6H, dmso-S), 3.46 (s, 6H, dmso-S), 3.23 (s, 6H, dmso-O), 3.21 (s, 12H, CH_3 dmso-O). ^{13}C NMR ($(CD_3)_2CO$, δ ppm): 196.0 (CO), 46.0 (CH_3, dmso-S), 45.6 (CH_3, dmso-S), 39.0 (CH_3, dmso-O), 38.4 (CH_3, dmso-O), 38.3 (CH_3, dmso-O). Selected IR absorptions (KBr, cm^{-1}): 2012 (ν_{CO}, s), 1128 (ν_{SO}, s, dmso-S), 927 (ν_{SO}, s, dmso-O), 481 (ν_{Ru-O}, m), 426 (ν_{Ru-S}, m).

*cis,cis,cis-[RuCl(CO)(dmso-O)$_2$(dmso-S)$_2$][PF$_6$] (**12**).* The procedure was very similar to that reported above for **11**, except that 1 eq of $AgPF_6$ (46.5 mg, 0.18 mmol) was used and the mixture was refluxed for 2.5 h. Yield of pale-yellow product (from 80 mg of **3**): 87 mg (76%). Elemental analysis calcd for [$C_9H_{24}ClF_6O_5PRuS_4$] (M_W: 622.00): C 17.3; H 3.88. Found: C 17.2; H 3.90. The complex is soluble in DMSO, CH_3COCH_3 and CH_3NO_2, partially soluble in CH_3OH and H_2O and insoluble in CH_3CH_2OH, $CHCl_3$, and CH_2Cl_2. Crystals suitable for X-ray analysis were obtained as described above for **11**. ^{1}H NMR (D_2O, δ ppm): 3.51 (s, 3H, CH_3 dmso-S), 3.36 (s, 3H, CH_3 dmso-S), 3.35 (s, 3H, CH_3 dmso-S), 3.25 (s, 3H, CH_3 dmso-S), 2.98 (s, 3H, CH_3 dmso-O), 2.96 (s, 6H, CH_3 dmso-O), 2.94 (s, 3H, CH_3 dmso-O). ($(CD_3)_2CO$, δ ppm): 3.49 (s, 3H, CH_3 dmso-S), 3.38 (s, 3H, CH_3 dmso-S), 3.31 (s, 3H, CH_3 dmso-S), 3.26 (s, 3H, CH_3 dmso-S), 3.09 (s, 3H, CH_3 dmso-O), 3.08 (s, 3H, CH_3 dmso-O), 3.07 (s, 6H, CH_3 dmso-O). ^{13}C NMR ($(CD_3)_2CO$, δ ppm): 197.20 (CO), 48.36 (CH_3, dmso-S), 45.27 (CH_3, dmso-S), 44.95 (CH_3, dmso-S), 43.38 (CH_3, dmso-S), 39.58 (CH_3, dmso-O), 38.86 (CH_3, dmso-O), 38.58 (CH_3, dmso-O), 38.36 (CH_3, dmso-O). Selected IR absorptions (KBr, cm^{-1}): 1996 (ν_{CO}, s), 1134 (ν_{SO}, s, dmso-S), 920 (ν_{SO}, s, dmso-O), 481 (ν_{Ru-O}, m), 424 (ν_{Ru-S}, m).

*cis,cis,trans-[Ru(CO)$_2$(dmso-O)$_2$(dmso-S)Cl][PF$_6$] (**13**).* To a 88.4 mg amount of *fac*-[$RuCl_2(CO)_3$(dmso-O)] (**8**) (0.26 mmol) dissolved in acetone (10 mL) were added DMSO (94 μL, 1.3 mmol, 5 equiv) and a slight excess of $AgPF_6$ (81.2 mg, 0.31 mmol, 1.2 equiv), and the mixture was stirred at ambient temperature for 3 h in the dark. It was then filtered over Celite to remove a dark brown precipitate (consisting of AgCl and other uncharacterized material) and the filter was extensively washed with acetone. The colorless solution was rotary-evaporated to an oil. Addition of ethanol (3 mL) afforded a solution from which colorless crystals of the product formed within a few days. During this period diethyl ether (2 mL) was slowly added dropwise to increase the crystal growth. The crystals (suitable for X-ray analysis) were eventually filtered, washed with ethanol and diethyl ether, and vacuum-dried. Yield 39.5 mg. An additional crop of product (29.0 mg) was obtained from the mother liquor repeating the same procedure as above, using a few drops of ethanol. Total yield: 46.0%. The same product was obtained also when the reaction was performed at reflux temperature and the Ag:Ru ratio was increased to 2; however, the growth in temperature led to an increase of the uncharacterized dark precipitate (responsible for the low yield of this preparation) that accompanies the formation of AgCl. The complex is soluble in DMSO, CH_3COCH_3, and CH_3NO_2; partially soluble in CH_3OH and H_2O; and insoluble in CH_3CH_2OH, $CHCl_3$, and CH_2Cl_2. Elemental analysis calcd for [$C_8H_{18}ClF_6O_5PRuS_3$] (M_W 571.88): C 16.8; H 3.17. Found: C 16.6; H 3.14. ^{1}H NMR ($(CD_3)_2CO$, δ ppm): 3.38 (s, 6H, CH_3 dmso-S), 3.13 (s, 6H, CH_3 dmso-O), 3.12 (s, 6H, CH_3 dmso-O); (D_2O, δ ppm): 3.39 (s, 6H, CH_3 dmso-S), 2.99 (s, 6H, CH_3 dmso-O), 2.98 (s, 6H, CH_3 dmso-O). ^{13}C NMR ($(CD_3)_2CO$, δ ppm): 191.3 (CO), 44.7 (CH_3, dmso-S), 39.3 (CH_3, dmso-O), 38.7 (CH_3, dmso-O). Selected IR absorptions (KBr, cm^{-1}): 2092 (ν_{CO}, vs), 2030 (ν_{CO}, vs), 1140 (ν_{SO}, s, dmso-S), 920 (ν_{SO}, s, dmso-O), 478 (ν_{Ru-O}, m), 424 (ν_{Ru-S}, m).

*trans,trans,trans-[OsCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**17**).* A 100 mg amount of *trans*-[$OsCl_2$(dmso-S)$_4$] (**14**) (0.17 mmol) was partially dissolved in 6 mL of methanol in a flask closed with a stopcock. The flask was first connected to a vacuum line and then to a reservoir of CO. After two vacuum/CO cycles were performed, the mixture was warmed to 45 °C for 24 h; within 6 h, all the solid dissolved, originating a deep yellow solution that became progressively paler. Rotary-evaporation to ca. 2 mL and addition of a few drops of diethyl ether induced the slow formation of a pale yellow precipitate, that was filtered, washed with cold methanol and diethyl ether and vacuum-dried. Yield: 49.0 mg (55%). Crystals of **17** suitable for X-ray were obtained from the mother liquor upon standing several days.

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Table 1. Crystallographic Data and Details of Refinement for the Ru(II) Complexes 11−13 and for the Os(II) Complexes 19 and 21

	11	12	13
empirical formula	$C_{11}H_{30}F_{12}O_6P_2RuS_5$	$C_9H_{24}ClF_6O_5PRuS_4$	$C_8H_{18}ClF_6O_5PRuS_3$
fw	809.66	622.01	571.89
cryst syst	monoclinic	monoclinic	triclinic
space group	$P\ 2_1/c$	$P\ 2_1/n$	$P\ \bar{1}$
a (Å)	14.4750(12)	10.8000(11)	7.5890(11)
b (Å)	10.3640(11)	14.7000(16)	10.9090(16)
c (Å)	21.043(3)	14.670(3)	12.924(3)
α (deg)			97.06(2)
β (deg)	108.137(10)	96.99(2)	100.352(12)
γ (deg)			100.84(2)
V (Å^3)	3000.0(6)	2311.7(6)	1020.0(3)
Z	4	4	2
D_{calcd} (g cm^{-3})	1.793	1.787	1.862
μ(Mo−Kα) (mm^{-1})	9.456	11.218	11.719
F(000)	1624	1248	568
θ range (deg)	4.59−52.54	4.27−62.34	4.75−53.91
no. of reflns collected	14978	16545	9290
no. of indepent reflns	3321	3510	2391
R_{int}	0.0710	0.0730	0.0512
no. of reflns ($I > 2\sigma(I)$)			
refined params	345	252	244
goodness-of-fit (F^2)	1.013	0.946	1.074
$R1$, $wR2$ ($I > 2\sigma(I)$)[a]	0.0552, 0.1659	0.0656, 0.1554	0.0706, 0.2103
residuals (e/Å^3)	0.784, −0.918	1.053, −1.105	1.040, −1.418

	19	21
empirical formula	$C_7H_{18}Cl_2O_4OsS_3$	$C_{7.50}H_{21}Cl_2O_4OsS_{3.50}$
fw	523.49	548.55
cryst syst	tetragonal	monoclinic
space group	$I4_1/a$	$P\ 2_1/c$
a (Å)	19.6180(12)	8.8040(11)
b (Å)		11.1840(16)
c (Å)	16.4140(10)	17.857(2)
α (deg)		
β (deg)		105.29(2)
γ (deg)		
V (Å^3)	6317.2(7)	1696.0(4)
Z	16	4
D_{calcd} (g cm^{-3})	2.202	2.148
μ(Mo−Kα) (mm^{-1})	22.098	8.266
F(000)	4000	1056
θ range (deg)	3.51− 63.97	2.75−26.61
no. of reflns collected	23480	2978
no. of indep reflns	2524	1747
R_{int}	0.0930	0.0125
no. of reflns ($I > 2\sigma(I)$)		
refined params	159	173
goodness-of-fit (F^2)	0.995	1.261
$R1$, $wR2$ ($I > 2\sigma(I)$)[a]	0.0554, 0.1296	0.0309, 0.0828
residuals (e/Å^3)	2.187, −1.359	0.702, −0.692

Elemental analysis calcd for [$C_7H_{18}Cl_2O_4OsS_3$] (M_W: 523.52): C 16.05, H 3.46. Found: C 16.1; H 3.48. ^{1}H NMR ($CDCl_3$, δ ppm): 3.46 (s, 12H, CH_3 dmso-S), 2.82 (s, 6H, CH_3 dmso-O). ^{13}C NMR ($CDCl_3$, δ ppm): 173.9 (1 CO), 43.9 (CH_3, dmso-S), 38.2 (CH_3, dmso-O). Selected IR absorptions (KBr, cm^{-1}): 1948 (ν_{CO}, vs), 1119 (ν_{SO}, s, dmso-S), 929 (ν_{SO}, s, dmso-O), 481 (ν_{Os-O}, m), 415 (ν_{Os-S}, m).

*trans,cis,cis-[OsCl$_2$(CO)$_2$(dmso-O)$_2$] (**18**).* A procedure very similar to that reported above for **17** was adopted, except that the mixture (200 mg of **14**, 0.35 mmol, in 20 mL of MeOH) was refluxed for 36 h under a CO atmosphere. Workup (as above) afforded 80 mg of the product (yield: 48%). Crystals suitable for X-ray analysis grew slowly from the concentrated mother liquor. Alternatively, to improve the yield, the final solution was rotary evaporated to an oil; repeated washing with diethyl ether eventually afforded a pale yellow solid that was filtered, washed with diethyl ether, and vacuum-dried. Yield: 104 mg (63%).

Elemental analysis calcd for [$C_6H_{12}Cl_2O_4OsS_2$] (M_W: 473.42): C 15.22; H 2.56 Found: C 15.3; H 2.62. ^{1}H NMR ($CDCl_3$, δ ppm): 2.92 (s, 12H, CH_3 dmso-O). ^{13}C NMR ($CDCl_3$, δ ppm): 172.1 (CO), 39.2

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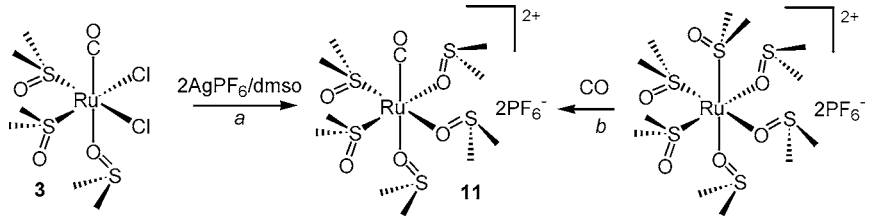
Scheme 2. Reaction Pathways Leading to *fac*-[Ru(CO)(dmso-O)$_3$(dmso-S)$_2$][PF$_6$]$_2$ (11)



(CH$_3$, dmso-O). Selected IR absorptions (KBr, cm^{-1}): 2025 (ν_{CO}, vs), 1941 (ν_{CO}, vs), 927 (ν_{SO}, s, dmso-O), 487 (ν_{Os-O}, m).

*cis,mer-[OsCl$_2$(CO)(dmso-S)$_3$] (**19**).* A 100 mg amount of *cis,fac*-[OsCl$_2$(dmso-S)$_3$(dmso-O)] (**15**) (0.17 mmol) was partially dissolved in 5 mL of methanol in a flask closed with a stopcock. The flask was first connected to a vacuum line and then to a reservoir of CO. After performing two vacuum/CO cycles, the mixture was warmed to 45 °C for 8 h; within 1 h all the solid dissolved, originating a colorless solution that was eventually rotary-evaporated to ca. 2 mL. Dropwise addition of diethyl ether until saturation led to the slow growth of colorless crystals that were filtered, washed with cold methanol and diethyl ether, and vacuum-dried. Yield: 57 mg (64%).

Elemental analysis calcd for [C$_7$H$_{18}$Cl$_2$O$_4$OsS$_3$] (M_W: 523.52): C 16.05; H 3.46. Found: C 16.1; H 3.44. ^{1}H NMR (CDCl$_3$, δ ppm): 3.70 (s, 6H, CH$_3$ dmso-S), 3.51 (s, 6H, CH$_3$ dmso-S), 3.47 (s, 6H, CH$_3$ dmso-S). ^{13}C NMR (CDCl$_3$, δ ppm): 169.81 (1 CO), 48.10 (CH$_3$, dmso-S), 45.96 (CH$_3$, dmso-S), 41.63 (CH$_3$, dmso-S). Selected IR absorptions (KBr, cm^{-1}): 1991 (ν_{CO}, vs), 1119 (ν_{SO}, br s, dmso-S), 424 (ν_{Os-S}, m).

*cis,trans,cis-[OsCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**20**).* As described in the text, compound **20** could not be isolated in pure form, but only as a 1:1 cocrystallized mixture (**21**) with its precursor **15**. Crystals of **21** were obtained by a procedure very similar to that reported above for **19**, except that the mixture was warmed at 35 °C, rather than 45 °C, for 8 h (a clear solution was obtained after ca. 2 h). Dropwise addition of diethyl ether until saturation to the concentrated solution led, upon standing overnight, to the growth of pale yellow crystals that were filtered, washed with cold methanol and diethyl ether, and vacuum-dried. Yield: 30 mg. After filtration of the crystals, the mother liquor was evaporated to an oil and then redissolved in 2 mL of ethanol. Addition of diethyl ether until saturation led to the slow formation of a white precipitate (20 mg) identified as **19** from the NMR spectrum.

Elemental analysis calcd for [C$_{15}$H$_{42}$Cl$_4$O$_8$Os$_2$S$_7$] (M_W: 1097.17): C 16.42; H 3.86. Found: C 16.6; H 3.78. ^{1}H NMR (CDCl$_3$, δ ppm): 3.65 (s, 6H, CH$_3$ dmso-S, **20@21**), 3.58 (s, 6H, CH$_3$ dmso-S, **15@21**), 3.55 (s, 6H, CH$_3$ dmso-S, **15@21**), 3.44 (s, 6H, CH$_3$ dmso-S, **15@21**), 3.35 (s, 6H, CH$_3$ dmso-S, **20@21**), 2.84 (s, 6H, CH$_3$ dmso-O, **20@21**), 2.77 (s, 6H, CH$_3$ dmso-O, **15@21**). ^{13}C NMR (CDCl$_3$, δ ppm): 172.72 (1 CO), 48.41 (CH$_3$, dmso-S, **20@21**), 47.97 (CH$_3$, dmso-S, **15@21**), 47.69 (CH$_3$, dmso-S, **15@21**), 45.07 (CH$_3$, dmso-S, **15@21**), 43.70 (CH$_3$, dmso-S, **20@21**), 38.86 (CH$_3$, dmso-O, **20@21**), 38.44 (CH$_3$, dmso-O, **15@21**). The ^{13}C resonances were assigned to **15** or to **20** through an HSQC spectrum, and confirmed by comparison with the ^{13}C NMR spectrum of a pure sample of compound **15**. Selected IR absorptions (KBr, cm^{-1}): 1967 (ν_{CO}, vs), 1123 (ν_{SO}, s, dmso-S), 920 (ν_{SO}, br s, dmso-O), 493 (ν_{Os-O}, m), 429 (ν_{Os-S}, m).

Crystallographic Measurements. Crystallographic data for compounds **11**−**13** and **19** were collected at room temperature on a Nonius DIP-1030H single crystal diffractometer (Mo−Kα radiation, λ = 0.71073 Å), whereas those of compound **21** were carried out at the X-ray diffraction beamline of synchrotron Elettra (Trieste) (at 100 K, λ = 0.9000 Å). Cell refinement, indexing and scaling of all the data sets were performed using programs Denzo and Scalepack.[13] All the structures were solved by direct methods and subsequent Fourier analyses,[14] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[14] In the crystals of **21** one ligand was found disordered and successfully interpreted as a mixture of CO and dmso-S with refined occupancies of 0.502(12) and 0.498(12), respectively. In other words, the crystals of **21** correspond to a 1:1 mixture of **15** and **20** (see text). Hydrogen atoms were placed at calculated positions. All the calculations were made using the WinGX System, Ver 1.80.05.[15] Crystal data and details of refinements are given in Table 1.

RESULTS AND DISCUSSION

Cationic Ru(II)-dmso Carbonyl Complexes. We found that treatment of the neutral monocarbonyl Ru(II) complex *cis,trans,cis*-[RuCl$_2$(CO)(dmso-O)(dmso-S)$_2$] (**3**) with two equivalents of AgPF$_6$ in the presence of DMSO leads to the replacement of both chlorides by O-bonded dmso molecules and to the isolation in good yield of the dicationic compound *fac*-[Ru(CO)(dmso-O)$_3$(dmso-S)$_2$][PF$_6$]$_2$ (**11**) (Scheme 2, path a).

The ^{1}H NMR spectrum of **11** in D$_2$O (immediately after dissolution) consists of five equally intense singlets, three in the region of dmso-O and two in that of dmso-S (ESI), and is thus consistent with the proposed structure. The sharpest peak at δ = 3.01 is assigned to the dmso-O trans to CO, that has enantiotopic methyls; the four coplanar dmso ligands − two bound through S and two through O − are pairwise equivalent but have diastereotopic methyls, whose resonances are slightly broadened by a small J_4 coupling (typically of the order of 0.5 Hz).[16] A similar spectrum was obtained in (CD$_3$)$_2$CO, where the complex is stable (ESI).

The solution structure of **11** was confirmed in the solid state by X-ray crystallography (Figure 1).

The Ru−O bond distance of the dmso-O trans to CO (2.088(8) Å), beside being shorter than those of the other two Ru−O bonds trans to dmso-S (2.115(9) and 2.097(7) Å), is remarkably shorter than in the precursor **3** (2.137(5) Å), suggesting that this ligand behaves as a better donor in **11** than in **3**. This finding might be explained by the increased positive charge of the complex and by the decreased steric hindrance in the equatorial plane (dmso-O is less bulky that Cl in the closeness of Ru). The presence of the *fac*-{Ru(dmso-O)$_3$} fragment in complex **11** is consistent with our previous observation that even in the absence of coordinated CO, the number of O-bonded dmso ligands in Ru-dmso compounds increases upon increasing the positive charge of the Ru(II) center (e.g., cfr *cis,fac*-[RuCl$_2$(dmso-O)(dmso-S)$_3$] with *fac*-[RuCl(dmso-O)$_2$(dmso-S)$_3$]$^+$ and *fac*-[Ru(dmso-O)$_3$(dmso-S)$_3$]$^{2+}$).[16] However, it should be noted that in the corresponding Ru(II)-nitrosyl complex with the same charge as **11**, i.e. [RuCl(dmso-O)$_4$(NO)]$^{2+}$, all four dmso ligands are bound through oxygen, suggesting that NO$^+$ removes more charge density from the Ru(II) center than CO.[17] In the nitrosyl complex the Ru−O(dmso) bond length trans to NO$^+$ (2.029(3) Å) is remarkably shorter than in **11**, due to the well-documented trans-shortening effect exerted by NO when coordinated trans to a σ-donor ligand.

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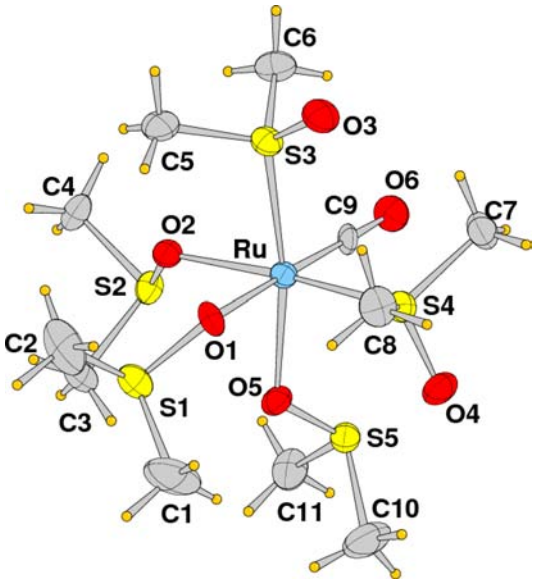
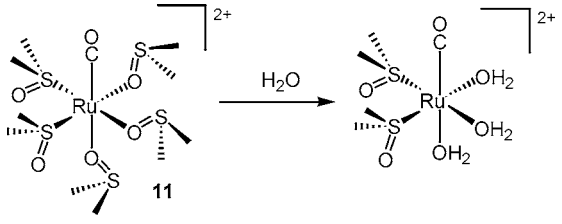


Figure 1. Thermal ellipsoid plot (40% probability) of the complex cation of **11**, *fac*-$[Ru(CO)(dmso\text{-}O)_3(dmso\text{-}S)_2]^{2+}$. Coordination bond distances (Å): Ru−C(9) 1.746(14), Ru−O(1) 2.088(8), Ru−O(2) 2.097(7), Ru−O(5) 2.115(8), Ru−S(3) 2.286(3), Ru−S(4) 2.286(3).

We found that compound **11** formed slowly also upon treatment of *fac*-$[Ru(dmso\text{-}O)_3(dmso\text{-}S)_3][PF_6]_2$ with 30 atm of CO at 25 °C in methanol solution (Scheme 2 path b, ca. 60% yield of **11** after 24 h). No formation of dicarbonyl species was observed under these conditions. This observation is consistent with the expectation that binding of CO to a cationic Ru(II) complex is an unfavorable process. Interestingly, an increase of the temperature to 50 °C led to the reduction of Ru(II) to Ru(0) and formation of $Ru_3(CO)_{12}$, also in the absence of any added base.[18]

When dissolved in water, complex **11** selectively releases the three dmso-O ligands generating within 24 h at ambient temperature the aqua species *fac*-$[Ru(CO)(dmso\text{-}S)_2(OH_2)_3]^{2+}$ (Scheme 3).

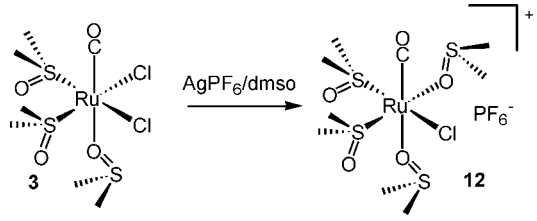
Scheme 3. Chemical Behavior of *fac*-$[Ru(CO)(dmso\text{-}O)_3(dmso\text{-}S)_2]^{2+}$ in Aqueous Solution



The occurrence of this process is evident from the time-resolved proton NMR spectra in D_2O (ESI): after 24 h, the five initial resonances of **11** are replaced by three resonances (integration ratio 1:1:3): two singlets at δ = 3.53 and 3.40 for the two equivalent dmso-S ligands (that have diastereotopic methyls) and the signal of free DMSO at δ = 2.72. This finding indicates that also in the cationic species the dmso-O ligands are more weakly bound than the dmso-S ligands and thus can be selectively replaced by the water molecules.

When the precursor **3** was treated with one equivalent of $AgPF_6$, the monocationic complex *cis,cis,cis*-$[RuCl(CO)(dmso\text{-}O)_2(dmso\text{-}S)_2][PF_6]$ (**12**), in which only one Cl is replaced by a dmso-O, was selectively obtained (Scheme 4).

Scheme 4. Reaction Pathway Leading to *cis,cis,cis*-$[RuCl(CO)(dmso\text{-}O)_2(dmso\text{-}S)_2][PF_6]$ (12)



Consistent with the all-cis geometry of **12**, eight well-resolved methyl resonances (four in the region of dmso-S and four in that of dmso-O) are found in its ^{13}C NMR spectrum (see the Supporting Information). Conversely, in the ^1H NMR spectrum (both in D_2O and in $(CD_3)_2CO$) two dmso-O resonances overlap (ESI). Also in this case the solution structure of **12** was confirmed in the solid state by X-ray crystallography (Figure 2).

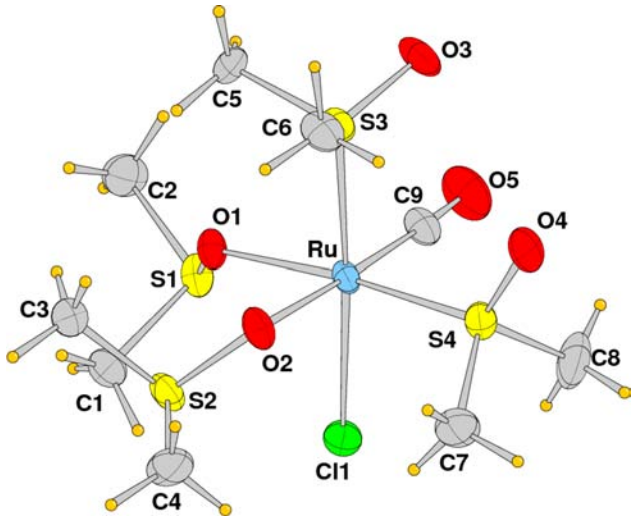


Figure 2. Thermal ellipsoid plot (40% probability) of the complex cation of **12**, *cis,cis,cis*-$[RuCl(CO)(dmso\text{-}O)_2(dmso\text{-}S)_2]^+$. Coordination bond distances (Å): Ru−C(9) 1.842(11), Ru−O(1) 2.103(5), Ru−O(2) 2.107(6), Ru−S(3) 2.295(3), Ru−S(4) 2.251(2), Ru−Cl(1) 2.412(3).

Although the coordination distances in the monocationic species **12** are less accurate than those measured in **11**, they appear to be slightly longer probably due to the different complex charge. The CO stretching frequency progressively increases on going from the neutral precursor **3** (1990 cm^{-1}) to the mono- and dicationic species **12** and **11** (1996 and 2012 cm^{-1}, respectively), consistent with the anticipated decrease of the π-back bonding contribution in the Ru−CO bond upon increasing the positive charge of the complex.

Similarly to what found for **11**, when dissolved in water compound **12** slowly releases the O-bonded dmso ligands; this process is accompanied also by partial dissociation of the Cl^- ligand. In fact, the ^1H NMR spectrum of a D_2O solution of **12** recorded 48 h after dissolution contains predominantly − in addition to the peak of free DMSO − two sets of singlets in the

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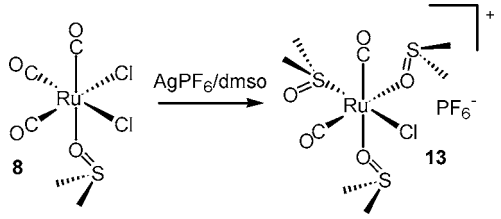
dmso-S region (ESI): four equally intense singlets (at δ = 3.57, 3.50, 3.39 and 3.40) are consistent with the presence of *cis,cis,cis*-$[RuCl(CO)(dmso\text{-}S)_2(OH_2)_2]^+$, whereas the two other singlets, which grow more slowly with time, belong to *fac*-$[Ru(CO)(dmso\text{-}S)_2(OH_2)_3]^{2+}$ (see above).

When the tricarbonyl precursor *fac*-$[RuCl_2(CO)_3(dmso\text{-}O)]$ (**8**) was treated with 1 equiv. of $AgPF_6$ in an acetone/DMSO mixture, a dicarbonyl complex of formula $[RuCl(CO)_2(dmso)_3][PF_6]$ (**13**) was obtained in moderate yield (Scheme 5).

Scheme 5. Reaction Pathway Leading to *cis,cis,trans*-$[Ru(CO)_2(dmso\text{-}O)_2(dmso\text{-}S)Cl][PF_6]$ (13)



The geometry of **13** and the binding mode of the dmso ligands were determined by NMR and IR spectroscopy. The two carbonyls give a single resonance in the ^{13}C NMR spectrum and two CO stretching bands in the IR spectrum: as a consequence, they must be equivalent and in cis geometry. The ^1H NMR spectrum of **13** features three equally intense singlets, one in the region of dmso-S and two in that of dmso-O. Overall, these data are consistent with the geometry *cis,cis,trans*-$[Ru(CO)_2(dmso\text{-}O)_2(dmso\text{-}S)Cl][PF_6]$ (the two equivalent dmso-O ligands have diastereotopic methyls). Thus, substitution of a Cl^- anion with a neutral dmso-O in **8** implied also the release of one CO ligand, that was replaced by another dmso (bound through S *trans* to Cl). The cation of **13** can be formally thought of as deriving from *trans,cis,cis*-$[RuCl_2(CO)_2(dmso\text{-}O)_2]$ (**10**) by replacing one of the two *trans* Cl ligands with a dmso-S. Consistent with the charge of the two species and with the nature of the Ru–CO bond, the CO stretching frequencies in **13** (2092 and 2030 cm^{-1}) are higher than in **10** (2054 and 1984 cm^{-1}).[1] Interestingly, removal of the second chlorido ligand from **8** could not be accomplished even under forcing conditions: treatment of **8** with two equivalents of $AgPF_6$ yielded compound **13**, also when the reaction was performed in hot DMSO.

X-ray crystallography confirmed the nature of compound **13** in the solid state (Figure 3). The coordination sphere in **13** presents geometrical values close to an ideal octahedron (max deviation observed in the S(3)–Ru–Cl(1) angle of 173.7(2)°) and the Ru–O bond distances (Ru–O(1) 2.124(13), Ru–O(2) 2.106(13) Å) are comparable within their esd's to the value found in the precursor **8** (2.095(4) Å).

In contrast with the cationic monocarbonyls **11** and **12**, compound **13** is remarkably labile in aqueous solution (where it is not very soluble): time-driven ^1H NMR spectra in D_2O showed that within 30 min after dissolution, the three singlets for the dmso ligands disappear completely and are replaced by the resonance for free DMSO. The complex is instead stable in noncoordinating solvents such as acetone.

Neutral Os(II)-dmso Carbonyl Complexes. As said in the Introduction, the chemistry of Os-dmso carbonyls is basically unexplored. To the best of our knowledge, only one such

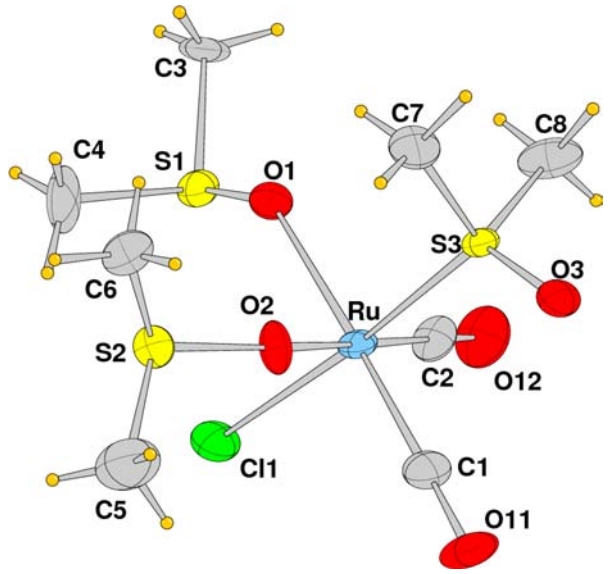
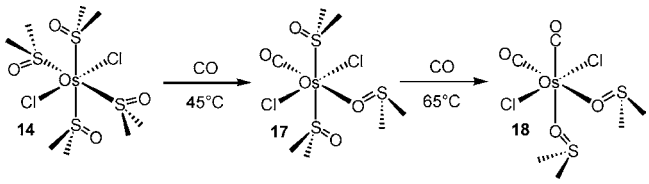


Figure 3. Thermal ellipsoid plot (40% probability) of the complex cation of **13**, *cis,cis,trans*-$[Ru(CO)_2(dmso\text{-}O)_2(dmso\text{-}S)Cl]^+$. Coordination bond distances (Å): Ru–C(1) 1.83(2), Ru–C(2) 1.87(2), Ru–O(2) 2.106(13), Ru–O(1) 2.124(13), Ru–S(3) 2.304(5), Ru–Cl(1) 2.390(6).

complex has been previously reported in the literature,[19] namely the Os(III) species $[nBu_4N]$*trans*-$[OsCl_4(CO)(dmso\text{-}O)]$ which is structurally similar to the corresponding Ru(III) analogue described by us.[20]

We found that the reactivity of *trans*-$[OsCl_2(dmso\text{-}S)_4]$ (**14**) toward CO is qualitatively similar to that of the corresponding Ru(II) complex **2**, i.e., CO replaces two adjacent dmso's in a stepwise manner, thereby inducing the S-to-O linkage isomerization of the trans-located dmso ligands (Scheme 6), even

Scheme 6. Reactivity of *trans*-$[OsCl_2(dmso\text{-}S)_4]$ (14) toward CO



though more forcing conditions are required. In fact, whereas treatment of *trans*-$[RuCl_2(dmso\text{-}S)_4]$ (**2**) with a CO atmosphere at room temperature yields the monocarbonyl species *trans,trans,trans*-$[RuCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**9**) in 3 h and the dicarbonyl product *trans,cis,cis*-$[RuCl_2(CO)_2(dmso\text{-}O)_2]$ (**10**) in 24 h, in the case of Os the preparation of the corresponding species *trans,trans,trans*-$[OsCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**17**) and *trans,cis,cis*-$[OsCl_2(CO)_2(dmso\text{-}O)_2]$ (**18**) from **14** required 24 h at 45 °C and 36 h at 65 °C (refluxing methanol), respectively. This finding is consistent with the well-known greater inertness of osmium compared to ruthenium.

The NMR and IR spectra of compounds **17** and **18** are very similar to those of the corresponding Ru complexes (ESI),[1] and will not be commented here. No isomerization from trans to cis geometry of the two chlorides was observed in the isolated products (according to NMR spectroscopy). However, as the

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yields of the isolated pure products were relatively modest (ca. 60%), the partial occurrence of this process cannot be excluded.

The molecular structure of the dicarbonyl complex **18** was confirmed by X-ray crystallography (Figure 4); however, since we could not manage to obtain crystals of suitable quality, no crystal data are reported for this analysis.

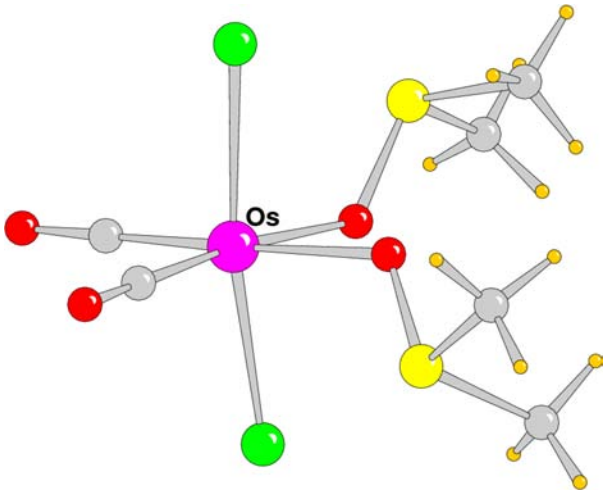
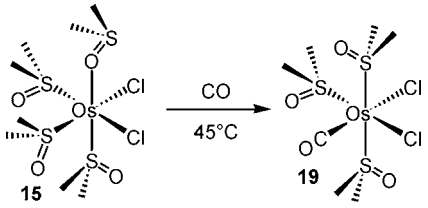


Figure 4. Low-quality molecular structure of complex *trans,cis,cis*-$[OsCl_2(CO)_2(dmso\text{-}O)_2]$ (**18**).

The reactivity of *cis,fac*-$[OsCl_2(dmso\text{-}O)(dmso\text{-}S)_3]$ (**15**) toward CO is instead somehow different from that of the corresponding Ru complex **1**. Treatment of **15** with CO in methanol at 45 °C for 8 h afforded a crystalline colorless compound that, based on analytical and spectroscopic data, was formulated as *cis,mer*-$[OsCl_2(CO)(dmso\text{-}S)_3]$ (**19**) (Scheme 7).

Scheme 7. Reaction Pathway Leading to *cis,mer*-$[OsCl_2(CO)(dmso\text{-}S)_3]$ (19)



Indeed the three equally intense singlets found in the ^{1}H NMR spectrum of **19** in the dmso-S region might be consistent also with a *fac* geometry for the complex, but this hypothesis would imply the existence of a dmso-S trans to CO, in contrast with all prior evidence that dmso is always bound through oxygen when trans to CO.[16] The nature of compound **19** was confirmed by the determination of the X-ray structure (Figure 5). Consistent with the weaker trans influence of Cl^- compared to dmso-S, the Os−S bond distance trans to Cl (2.273(3) Å) is shorter than the other two (2.369(3) and 2.340(3) Å).

For comparison, treatment of the Ru(II) precursor **1** with CO at ambient temperature afforded either *cis,trans,cis*-$[RuCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**3**, from methanol) or *cis,cis,cis*-$[RuCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**4**, from chloroform), whereas the Ru(II) monocarbonyl complex isostructural to **19**, i.e., **5**, was observed to form in solution upon isomerization from both **3** and **4**, but it was never isolated.[1,2]

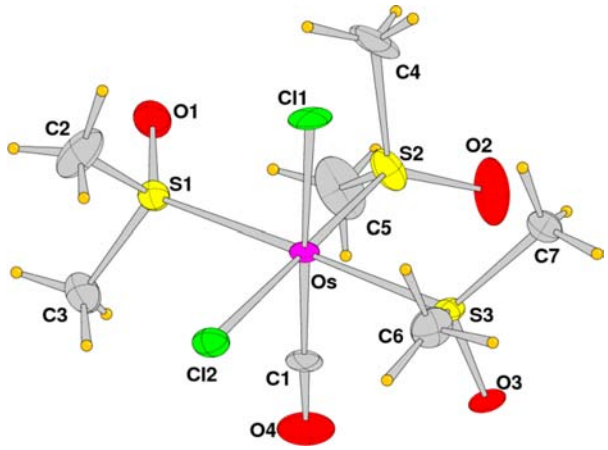


Figure 5. Thermal ellipsoid plot (40% probability) of *cis,mer*-$[OsCl_2(CO)(dmso\text{-}S)_3]$ (**19**). Coordination bond distances (Å): Os−C(1) 1.870(14), Os−S(1) 2.340(3), Os−S(2) 2.273(3), Os−S(3) 2.369(3), Os−Cl(1) 2.412(3), Os−Cl(2) 2.412(3).

Conversely, the only known Ru(II)-tmso monocarbonyl complex (tmso = tetramethylene sulfoxide), *cis,mer*-$[RuCl_2(CO)(tmso\text{-}S)_3]$, has the same meridional geometry as **19**,[21] thus confirming the greater propensity of tmso to bind to Ru(II) through the S atom compared to dmso.[22]

Intrigued by these findings, we investigated the above reaction between **15** and CO further, and found that when it was performed at lower temperature (35 °C rather than 45 °C) a pale-yellow crystalline compound (**21**) could be isolated from the concentrated solution. According to the IR spectrum, compound **21** was tentatively formulated as a monocarbonyl Os-dmso complex (single CO stretching band at 1967 cm^{-1}) containing both dmso-S and dmso-O ligands. We also observed that, after filtration of **21**, complex **19** could be isolated from the concentrated mother liquor and its amount increased − and that of **21** correspondingly decreased − upon increasing the reaction time. This finding confirmed that **19** is the thermodynamic product of the reaction between **15** and CO under moderate conditions and that **21** is a reaction intermediate. The ^{1}H NMR spectrum of **21** in $CDCl_3$ (solution obtained by dissolving single crystals selected under the microscope) was quite intriguing, as it consisted of seven equally intense singlets in the dmso region, four of which coincident with the resonances of the precursor **15** (ESI).[10] The three remaining singlets (δ = 3.65, 3,35 and 2.84) were consistent with the presence in solution of the *cis,trans,cis*-$[OsCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**20**) species (analogous to the Ru(II) compound **3**). The same NMR spectrum was observed for different batches of **21**, obtained by changing the reaction time (for reaction times longer than 8 h the precipitate of **21** was contaminated by small amounts of **19**). The NMR spectrum of **21** changed slowly with time: basically, the resonances of **20** were progressively replaced by those of **19** (confirming that **19** is thermodynamically more stable), and the resonances of **15** by those of its linkage isomer *cis*-$[OsCl_2(dmso\text{-}S)_4]$ (**16**).[10] In addition, some dissociation of dmso also occurred, making the aged spectrum quite complicated.

Single crystal X-ray analysis confirmed that **21** is a mixture of the precursor **15** and of its monocarbonyl product **20** that cocrystallize spontaneously in a 1:1 ratio. The two complexes in the crystal, each one with occupancy 0.5, are identical (also in

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terms of orientation of the dmso ligands) except for the position trans to dmso-O, which is occupied by a dmso-S in **15** and by a CO in **20** (Figure 6). The geometrical parameters of

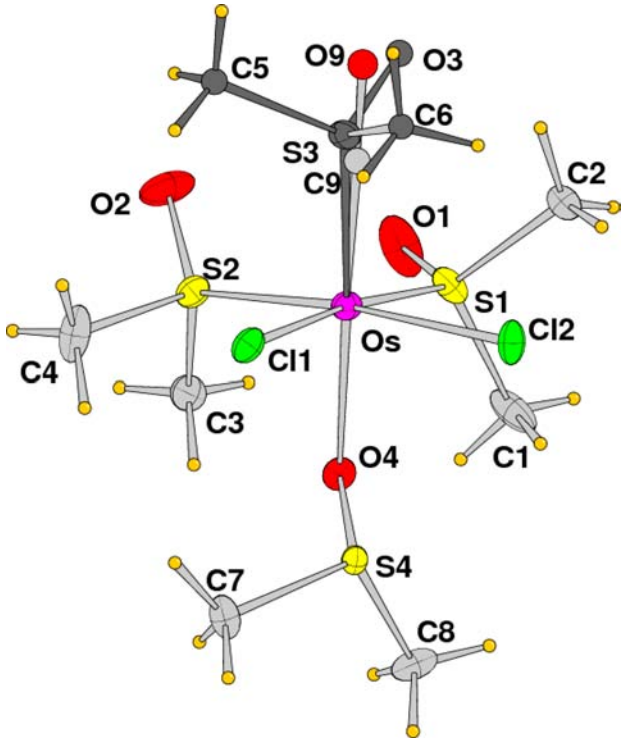


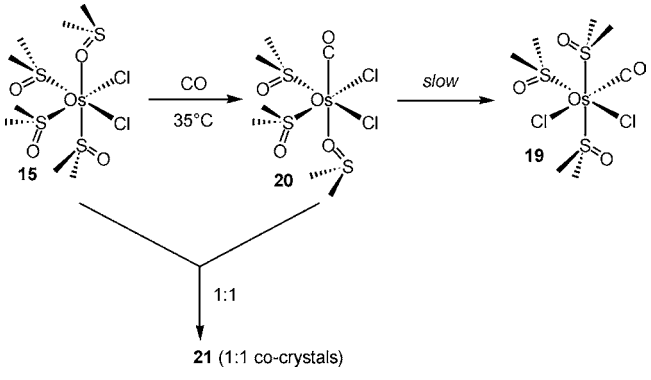
Figure 6. Thermal ellipsoid plot (40% probability) of complex *cis,trans,cis*-$[OsCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**20**) spontaneously cocrystallized in 1:1 ratio with its precursor **15** (with the dmso-S indicated in gray in place of the CO). Coordination bond distances (Å): Os–C(9) 1.82(3), Os–O(4) 2.118(5), Os–S(1) 2.264(3), Os–S(2) 2.263(2), Os–S(3) 2.235(5), Os–Cl(1) 2.429(2), Os–Cl(2) 2.430(2).

20@21 are closely comparable to those found by us for the Ru analog **3**,[1] whereas the structural features of **15@21** compare well with those found by us in the crystals of pure **15**.[10]

The reactivity of **15** toward CO under the relatively mild conditions investigated here is summarized in Scheme 8.

The kinetic product **20** is formed first and it then isomerizes to the more stable **19**. At 35 °C the conversion of **20** to **19** is

Scheme 8. Reactivity of *cis,fac*-$[OsCl_2(dmso\text{-}O)(dmso\text{-}S)_3]$ (15) toward CO Leading to the Isolation of the Monocarbonyl Isomeric Species 20 (exclusively as a co-crystallized 1:1 mixture with 15) and 19



relatively slow, thus **20** builds-up in the solution and can spontaneously cocrystallize in a 1:1 ratio with the residual precursor generating **21**. Both **15** and **20** are limiting reagents for the formation of **21**. Thus, the formation of the cocrystals of **21** is a rare case in which a 1:1 mixture of a precursor (**15**) and of its product (**20**) is less soluble than each of them.

CONCLUSIONS

We described here the preparation and structural characterization of three new cationic Ru(II)-dmso carbonyls. The two monocarbonyl species *fac*-$[Ru(CO)(dmso\text{-}O)_3(dmso\text{-}S)_2][PF_6]_2$ (**11**) and *cis,cis,cis*-$[RuCl(CO)(dmso\text{-}O)_2(dmso\text{-}S)_2][PF_6]$ (**12**) were obtained from the neutral monocarbonyl precursor *cis,trans,cis*-$[RuCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**3**) upon stepwise replacement of the chlorides with dmso, that binds in each case through the oxygen atom. The dicarbonyl cationic complex *cis,cis,trans*-$[Ru(CO)_2(dmso\text{-}O)_2(dmso\text{-}S)Cl][PF_6]$ (**13**) was instead obtained upon treatment of the neutral tricarbonyl precursor *fac*-$[RuCl_2(CO)_3(dmso\text{-}O)]$ (**8**) with $AgPF_6$ in the presence of DMSO. Even though the dicationic tricarbonyl aqua species *fac*-$[Ru(CO)_3(OH_2)_3]^{2+}$ has been prepared and structurally characterized as BF_4^- salt,[23] in this case we were unable to prepare the analogous dicationic dmso compound. First of all we succeeded in removing only one of the two Cl^- anions from **8** (even using an excess of $AgPF_6$); in addition, its replacement with a neutral dmso-O ligand implied also the substitution of one CO ligand by another dmso (that binds through S *trans* to Cl). Most likely, by analogy with the behavior of *fac*-$[Ru(CO)_3(OH_2)_3]^{2+}$,[23] the intermediate transient species *fac*-$[RuCl(CO)_3(dmso\text{-}O)_2]^+$ undergoes nucleophilic attack by adventitious water in the solvent yielding *fac*-$[RuCl(CO)_2(COOH)(dmso\text{-}O)_2]$, followed by CO_2 elimination to give the hydride *fac*-$[RuCl(CO)_2(H)(dmso\text{-}O)_2]$ that eventually yields the final product **13**. The preparation of **13** is accompanied also by the rapid formation of decomposition products (an uncharacterized black material) responsible for the global low yield.

As shown by the hydrolytic processes monitored by ^1H NMR spectroscopy in D_2O, and by analogy with the behavior of their neutral parent compound **3**, we anticipate that complexes **11** and **12** will behave as efficient precursors for the preparation of substituted cationic monocarbonyl derivatives by stepwise reaction with neutral σ-donors, as most likely the dmso-O ligands will be replaced under milder conditions than Cl (when present) and dmso-S ligands. Conversely, as both the two dmso-O ligands and the dmso-S ligand in the dicarbonyl species **13** are replaced with comparable rates by water molecules, stepwise substitution with neutral σ-donors is unlikely to occur easily; nevertheless, this complex might be expected to react efficiently with tridentate facial ligands yielding dicarbonyl species containing the *fac*-$\{RuCl(CO)_2\}^+$ fragment.

In the second part of this work we described four unprecedented mono- and dicarbonyl Os(II)-dmso derivatives, namely: *trans,trans,trans*-$[OsCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**17**), *trans,cis,cis*-$[OsCl_2(CO)_2(dmso\text{-}O)_2]$ (**18**), *cis,mer*-$[OsCl_2(CO)(dmso\text{-}S)_3]$ (**19**), and *cis,trans,cis*-$[OsCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**20**). Each one of them is structurally similar to an already known Ru(II) analog. Overall we found that the reactivity of the Os(II)-dmso precursors *trans*-$[OsCl_2(dmso\text{-}S)_4]$ (**14**) and *cis,fac*-$[OsCl_2(dmso\text{-}O)(dmso\text{-}S)_3]$ (**15**) toward CO is qualitatively similar to that of the corresponding Ru(II) complexes, even though – in agreement

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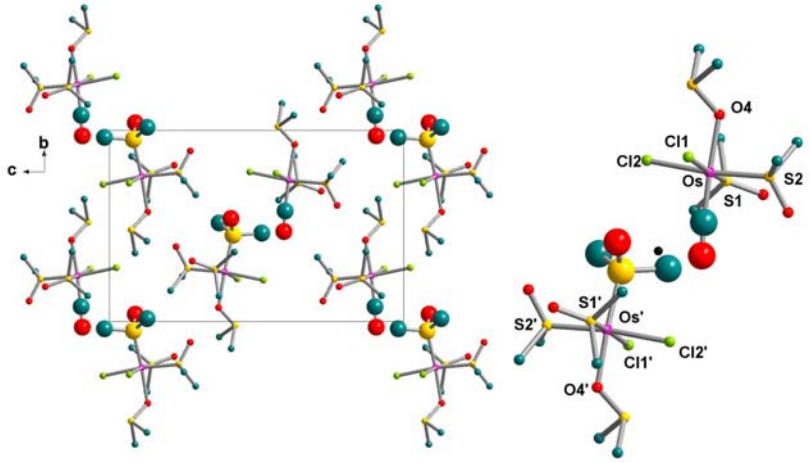

Figure 7. Left: crystal packing of **21** showing how each pair of complexes **15** and **20** is related by a center of symmetry that leads to a 50:50 disorder state for dmso-S3 and carbonyl C9 (see also Figure 6). Only one disordered group in each complex is shown for clarity. Right: detail of the centrosymmetric arrangement in the crystal packing of **21**, with the center of symmetry indicated with a black dot.

with the expected greater inertness of Os(II) − more forcing reaction conditions were required. As for ruthenium, also in the case of osmium coordination of CO induced the selective S-to-O linkage isomerization of the dmso *trans* to it. However, consistent with the greater propensity of Os(II) to bind dmso through S compared to Ru(II) (i.e., Os(II) is softer than Ru(II)), we found that the most stable monocarbonyl derivative of **15** is *cis,mer*-$[OsCl_2(CO)(dmso\text{-}S)_3]$ (**19**), and the stereoisomer *cis,trans,cis*-$[OsCl_2(CO)(dmso\text{-}O)(dmso\text{-}S)_2]$ (**20**) is only a kinetic product.

The spontaneous cocrystallization of compound **20** with its precursor **15** in 1:1 ratio to give **21** deserves some additional comment. By far, most of the examples of cocrystals reported in the literature concern organic compounds used as pharmaceuticals (the so-called pharmaceutical cocrystals).[24−26] In fact, the engineering of cocrystals of an active pharmaceutical ingredient (API) with an appropriate counter-molecule (the pharmaceutical cocrystal former) is seen as a way for improving the physicochemical properties of the APIs and for extending the IP protection. There has been recent debate in the community of crystallographers about the definition of what is a cocrystal.[27] Indeed, compound **21** described here strictly follows the definition given by Andrew Bond of a cocrystal as a "multicomponent molecular crystal".[28]

The examples of cocrystallization of coordination compounds most often concern mixtures of complexes that differ for very similar ligands (e.g., Cl vs Br).[19,29] Typically, in those cases, the ratio between the two compounds is variable and depends on the reaction and crystallization conditions, and thus the phenomenon is more frequently described in terms of disorder rather than cocrystallization. In our opinion the formation of the cocrystals of **21** has two unusual features: (i) the two compounds **15** and **20** cocrystallize exactly in a 1:1 ratio, and (ii) they differ for a pair of ligands that are quite different from one another (CO vs dmso-S). The lower solubility of the 1:1 mixture compared to the single components is probably due to the optimal packing obtained in the cocrystal of **21** because, as shown in Figure 7, there are apparently no specific intermolecular interactions between the two molecular species **15** and **20** in the crystal.

Overall, we are confident that also compounds **17**−**20** represent a contribution to expand the pool of complexes bearing some easily replaceable dmso ligands to be used as well-behaved precursors in inorganic synthesis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF with details of X-ray data collection and refinement for compounds **11**−**13**, **19**, and **21**. ^1H and ^{13}C NMR spectra of the reported complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Maurizio Prato on the occasion of his "C60th" birthday.

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