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Unexpected Formation of a Weak Metal−Metal Bond: Synthesis, Electronic Properties, and Second-Order NLO Responses of Push−Pull Late−Early Heteronuclear Bimetallic Complexes with $W(CO)_3$(1,10-phenanthroline) Acting as a Donor Ligand

Maddalena Pizzotti,* Renato Ugo, Claudia Dragonetti, and Elisabetta Annoni

Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università di Milano, Unità di ricerca dell'INSTM dell'Università di Milano e Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM), Via Venezian 21, 20133 Milano, Italy

Francesco Demartin

Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Via Venezian 21, 20133 Milano, Italy

Patrizia Mussini

Dipartimento di Chimica Fisica ed Elettrochimica, Via Venezian 21, 20133 Milano, Italy

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In attempts to bridge the complex $[W(CO)_3(phen)(pyz)]$ (phen = 1,10-phenanthroline; pyz = pyrazine) to acceptor centers, either soft centers such as *cis*-$M(CO)_2Cl$ (M = Rh(I), Ir(I)) and *fac*-$M(CO)_3Cl_2$ (M = Ru(II), Os(II)) or hard centers such as BF_3, the pyrazine ligand is lost, while the fragment $W(CO)_3$(phen) behaves as a σ-donor base with the unexpected formation of heteronuclear early−late bimetallic compounds with a weak metal−metal bond, as confirmed by the easy substitution of $W(CO)_3$(phen) by soft ligands (PPh_3, CO, pyridine). The X-ray structures of $[(CO)_3(phen)W$-*cis*-$Ir(CO)_2Cl]$ and $[(CO)_3(phen)W$-*fac*-$Os(CO)_3Cl_2]$ confirm a single metal−metal bond with an halogen bridging asymmetrically the two metallic moieties and with the tungsten atom achieving a distorted (6 + 1) octahedral coordination. All the heteronuclear bimetallic complexes investigated show in their electronic spectra a new solvatochromic absorption band at around 385−450 nm in addition to the MLCT ($W \rightarrow \pi^*_{phen}$) absorption band typical of $[W(CO)_3(phen)L]$ complexes (L = CO, pyz, CH_3CN) and an increased, in comparison to $[W(CO)_4(phen)]$, negative nonlinear (NLO) second-order emission working with the EFISH technique with an incident wavelength of 1.907 μm. The increase is due to an additional negative contribution of the new absorption band at around 385−450 nm, as shown by a solvatochromic investigation.

Introduction

In the past few years organometallic compounds, studied as molecular systems with potential second-order NLO properties, have shown a wide range of advantages[1] due to the control and tuning of the electronic properties of the metal and consequently of the highly polar metal to ligand or ligand to metal charge-transfer processes. Heteronuclear bimetallic complexes, in which the electron-accepting and -donating properties of two organometallic fragments are combined in order to generate a new kind of push−pull system, are quite interesting NLO chromophores.[2−4]

Recently we reported[3] the synthesis, electronic properties, and second-order NLO response of new push−pull asymmetrical bimetallic heteronuclear complexes with pyrazine (pyz) and *trans*-1,2-bis(4-pyridyl)ethylene (BPE) as polarizable linkers (L) between the $W(CO)_5$ moiety acting, in the excitation process, as donor group[5] and *cis*-$Rh(CO)_2Cl$, *cis*-$Re(CO)_4Cl$, or BF_3 acting as the

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acceptor group.[6-8] In these push−pull systems the MLCT (metal to ligand charge transfer) process (W → π^*_L), the origin of the second-order NLO response, remains localized on the part of the linker L close to the push $W(CO)_5$ group.[3]

To increase the second-order NLO response of these kinds of bridged heteronuclear bimetallic systems, we investigated the substitution of $W(CO)_5$ as push group with $W(CO)_3(phen)$, which should act as a better donor due to a more facile MLCT transition (W → π^*_L). In fact, [$W(CO)_4$(phen)] (phen = 1,10-phenanthroline) is reported to have, in its visibile spectrum, an MLCT band at lower energies (between 470 and 500 nm) together with a higher dipole moment (between 7 and 8 D) with respect to [$W(CO)_5$(pyz)] (MLCT at about 400 nm and dipole moment of about 4 D).[9] In attempts to bridge the complex [$W(CO)_3$(phen)(pyz)] to an organometallic acceptor fragment such as *cis*-$Ir(CO)_2Cl$, the pyrazine bridge is lost, while in parallel the fragment $W(CO)_3$(phen) behaves as a σ-donor base with the unexpected formation of a new compound with an early−late (W−Ir) heteronuclear metal−metal bond. The aim of this work was thus to investigate in detail the synthesis, electronic properties, and second-order NLO responses of a series of these new asymmetrical early-late heterobimetallic complexes with a W−M metal−metal bond (M = Ir(I), Rh(I), Os(II), Ru(II), or even BF_3) and to study their reactivity toward basic ligands of different softness (CO, PPh_3, pyridine) in order to evaluate the strength of the W−M interaction, in comparison to classical early−late heteronuclear metal−metal bonds.

Experimental Section

General Comments. $W(CO)_6$, $RhCl_3{\cdot}3H_2O$, $RuCl_3{\cdot}3H_2O$, $OsCl_3{\cdot}3H_2O$, 1,10-phenanthroline, and $BF_3{\cdot}OEt_2$ were purchased from Sigma-Aldrich and were used without further purification. The dimers [*cis*-$Rh(CO)_2Cl]_2$ and [*fac*-$M(CO)_3Cl_2]_2$ (M = Ru, Os) were prepared according to well-known syntheses;[10] [$Re(CO)_4Cl]_2$,[11] [$W(CO)_4$(phen)],[12] [*fac*-$W(CO)_3$(phen)(CH_3CN)],[13] and [*cis*-$Ir(CO)_2Cl$(pyz)][14] were prepared as described. [*cis*-$Re(CO)_4Cl$(THF)] was prepared in situ from the dimer [$Re(CO)_4Cl]_2$ dissolved in THF. [$W(CO)_5$(THF)] was prepared by photochemical activation of [$W(CO)_6$] in THF.[15]

All reactions and workups of the reaction mixtures were carried out under a nitrogen atmosphere, and all solvents were dried over molecular sieves (4 Å) prior to use. ^1H NMR spectra were obtained on a Bruker Advance DRX 300 instrument, electronic spectra on a JASCO V-530 spectrophotometer, fluorescence spectra on a JASCO FP-777 spectrofluorimeter, and IR spectra on a JASCO FT-IR 420 instrument. Dipole moments (μ) were obtained in $CHCl_3$ solution, using a WTW-DM01 dipole meter (dielectric constant) coupled with a Pulfrich Zeiss PR2 refractometer (refractive index), according to the Guggenheim method.[16] Elemental analyses were carried out at the Dipartimento di Chimica Inorganica, Metallorganica e Analitica of the Milan University and repeated, particularly when not enough satisfactory and reproducible, by an external microanalytical laboratory (REDOX Microanalytical Laboratory-Cologno Monzese, Milano, Italy).

Determination of the Second-Order NLO Response by the EFISH Technique and by the Solvatochromic Method. EFISH (electric field second harmonic generation) measurements[17] of β_λ, the projection of the quadratic hyperpolarizability tensor β along the dipole moment axis working with an incident wavelength λ, were carried out at the Dipartimento di Chimica Inorganica, Metallorganica e Analitica of Milan University on $CHCl_3$ solutions of different concentrations (10^{-3}−10^{-4} M), working at a nonresonant fundamental incident wavelength of 1.907 μm, obtained using a Q-switched, mode-locked Nd^{3+}:YAG laser connected to a Raman shift with pulse durations of 15−90 ns at a 10 Hz repetition rate. All experimental EFISH $\beta_{1.907}$ values are defined according to the "phenomenological" convention.[18]

The quadratic hyperpolarizability along the charge-transfer direction, β_{CT}, was determined by the solvatochromic method, taking into account the solvatochromic shift of the two major absorption bands in various solvents (toluene, ethyl ether, chloroform, ethyl acetate, THF, dichloromethane, 1,2-dichloroethane, acetone, and dimethylformamide; see Table 4). While the heteronuclear bimetallic compounds investigated show a fluorescent emission (Table 3), the solvatochromic shifts of this emission do not give the linear relationships expected according to the most applied theoretical approach.[19] Therefore, the cavity radius (a) was not indirectly evaluated by a parallel use of both absorption and emission solvatochromism but was evaluated using the traditional molecular weight approximation.[19] The acceptability of this latter choice was based on the evidence that the calculated values are within the range of the values of a determined from structural data. For instance, for pseudolinear molecules the radius a has been generally determined either by adding 0.5 Å to the half length of the molecule or as 0.7 times the length of the molecule (see for instance ref 7 reported in ref 19). By these two approaches the calculated values of a are 5.97 and 7.66 Å, respectively, for **1** (to be compared to 7.12 Å calculated from the molecular weight) and 6.07 and 7.80 Å, respectively, for **4** (to be compared to 7.30 Å calculated from the molecular weight). In conclusion, for the complexes investigated in this work, we have an acceptable convergence of values of a calculated either from molecular weight or from structural data.

The quadratic hyperpolarizability tensor β_{CT} along the charge-transfer axis of the MLCT (metal to ligand charge transfer) transitions controlling the NLO response was calculated according to the Oudar two-level equation[20]

$$\beta_{CT} = \frac{3}{2h^2c^2}\frac{\nu_a{}^2 r_{eg}{}^2 \Delta\mu_{eg}}{(\nu_a{}^2 - \nu_L{}^2)(\nu_a{}^2 - 4\nu_L{}^2)} \tag{1}$$

where r_{eg} is the transition dipole moment related to the

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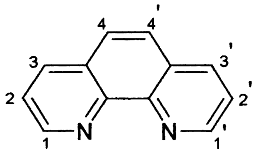
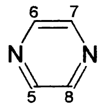
oscillator strength f of the absorption band, ν_a is the frequency of the MLCT absorption band, ν_L is the frequency of the fundamental incident radiation (in our case 1.907 μm), and $\Delta\mu_{eg}$ is the variation of the dipole moment between excited and ground states.[19]

Synthesis of the Complexes. The numbering used in the attribution of the ^{1}H NMR signals of the 1,10-phenanthroline (phen) and pyrazine (pyz) complexes is





[*fac*-W(CO)$_3$(phen)(pyz)]. To a solution of pyrazine (216 mg, 2.7 mmol) in THF (5 mL) at 0−5 °C (ice bath) was added dropwise a blue solution of [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] (140 mg, 0.27 mmol) in THF (20 mL) over 5 min. The reaction mixture changed color immediately from blue to violet and was stirred for 15 min. Then small portions of *n*-hexane were added, alternating with slow evaporation of the solvent. Finally the violet powder was filtered off, washed with *n*-hexane, and dried in vacuo (yield 36%). This compound must be stored under nitrogen in the dark. IR (CH$_2$Cl$_2$; cm^{-1}): ν_{CO} 1898 (s), 1786 (br). ^{1}H NMR (CD$_2$Cl$_2$; δ (ppm)): 9.68 (dd, 2H, $H_1H_{1'}$), 8.49 (dd, 2H, $H_3H_{3'}$), 8.15 and 8.22 (2m, 4H, $H_5H_6H_7H_8$), 7.99 (s, 2H, $H_4H_{4'}$), 7.84−7.88 (m, 2H, $H_2H_{2'}$). Visible spectrum (CH$_2$Cl$_2$; λ_{max} (nm) (log ϵ)): 356 (2.87), 511 (3.09), 578 (3.28). Anal. Found (calcd) for $C_{19}H_{12}N_4O_3W$: C, 42.9 (43.2); H, 2.29 (2.27); N, 9.96 (10.1).

[(CO)$_3$(phen)W(pyz)W(CO)$_3$(phen)]. This compound was prepared by following the above procedure for the synthesis of the monomer [*fac*-W(CO)$_3$(phen)(pyz)] but using a molar ratio of 1:1. After 10 min a violet dimer precipitated from the solution. It was filtered off and washed with xylene (yield 47%). This compound must be stored in the dark. IR (Nujol; cm^{-1}): ν_{CO} 1877 (vs), 1792 (vs), 1758 (s). ^{1}H NMR (CD$_2$Cl$_2$; δ (ppm)): 9.47 (dd, 2H, $H_1H_{1'}$), 8.59 (s, 4H, $H_5H_6H_7H_8$), 8.49 (dd, 2H, $H_3H_{3'}$), 8.0 (s, 2H, $H_4H_{4'}$), 7.79−7.86 (m, 2H, $H_2H_{2'}$). Anal. Found (calcd) for $C_{34}H_{20}N_6O_6W_2$: C, 41.6 (41.8); H, 2.09 (2.05); N, 8.61 (8.61).

[(CO)$_3$(phen)W-*cis*-Rh(CO)$_2$Cl] 1. To a solution of [Rh(CO)$_2$Cl]$_2$ (50 mg, 12.8 mmol) in THF (5 mL) at 0−5 °C (ice bath) was added dropwise a blue solution of [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] (125 mg, 25.6 mmol) in THF (30 mL) over 5 min. After 15 min small portions (3 mL) of *n*-hexane were added to the brown solution, alternating with slow evaporation of the solvent. Finally the suspension of the brown powder was filtered off under a nitrogen atmosphere, washed with *n*-hexane, and dried in vacuo (yield 40%). Compound **1** must be stored under nitrogen in the dark. IR (CHCl$_3$; (cm^{-1})): ν_{CO} 2063 (s), 1997 (s), 1929 (s), 1834 (s); ν_{RhCl} (Nujol) 287 (w). ^{1}H NMR (CDCl$_3$; δ (ppm)): 9.51 (dd, 2H, $H_1H_{1'}$), 8.59 (dd, 2H, $H_3H_{3'}$), 8.07 (s, 2H, $H_4H_{4'}$), 7.90−7.95 (m, 2H, $H_2H_{2'}$). Visible spectrum by deconvolution (CHCl$_3$; λ_{max} (nm) (log ϵ)): 392 (3.86), 444 (3.65), 517 (3.85). Anal. Found (calcd) for $C_{17}H_8N_2O_5ClWRh$: C, 32.1 (31.8); H, 1.29 (1.25); N, 4.32 (4.36).

Compound **1** was also prepared by starting from [Rh(CO)$_2$Cl(pyz)] instead of [Rh(CO)$_2$Cl]$_2$ and [*fac*-W(CO)$_3$(phen)(CH$_3$CN)], following the same procedure (yield 37.5%).

[(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] 2. To a yellow solution of [*cis*-Ir(CO)$_2$Cl(pyz)] (93.1 mg, 0.256 mmol) in THF (5 mL) at 0−5 °C (ice bath) was added dropwise a deep blue solution of [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] (125 mg, 0.256 mmol) in THF (30 mL) over 5 min. After 10 min the dark brown solution was evaporated to dryness and the violet-black residue was dissolved in 8 mL of THF; after filtration of a small insoluble residue, a brown powder was precipitated by adding successively small portions of *n*-hexane followed by slow evaporation of the solvent. The final suspension of the brown powder was filtered under a nitrogen atmosphere and washed with *n*-hexane (yield 25%). Compound **2** must be stored under nitrogen in the dark. IR (CH$_2$Cl$_2$; (cm^{-1})): ν_{CO} 2054 (s), 1980 (s), 1938 (m), 1840 (br). ^{1}H NMR (CDCl$_3$; δ (ppm)): 9.50 (dd, 2H, $H_1H_{1'}$), 8.60 (dd, 2H, $H_3H_{3'}$), 8.09 (s, 2H, $H_4H_{4'}$), 7.93−7.97 (m, 2H, $H_2H_{2'}$). Visible spectrum (CHCl$_3$; λ_{max} (nm) (log ϵ)): 385 (3.74), 503 (3.59). Anal. Found (calcd) for $C_{17}H_8N_2O_5ClWIr$: C, 28.0 (27.9); H, 1.11 (1.09); N, 3.80 (3.83).

[(CO)$_3$(phen)W-*fac*-Ru(CO)$_3$Cl$_2$] 3. To a solution of [Ru(CO)$_3$Cl$_2$]$_2$ (109 mg, 0.213 mmol) in THF (10 mL) at 0−5 °C (ice bath) was added dropwise a blue solution of [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] (209 mg, 0.429 mmol) in THF (45 mL). After 1 h the temperature was raised to room temperature, and after 5 h the suspension was filtered off. Then the solvent was partially removed under reduced pressure and compound **3** precipitated, by addition of *n*-hexane, as a brown powder together with some amount of [(CO)$_3$(phen)W-*fac*-Ru(CO)$_3$Cl$_2$]·THF with one molecule of THF coordinated, as evidenced by the high number of carbonyl bands in the IR spectrum of the mixture (Table 1) and by its ^{1}H NMR spectum.[21] However, in CHCl$_3$ solution the mixture slowly rearranged to compound **3** (about 24 h), which was recovered by evaporation to dryness (yield 80%). IR (CHCl$_3$; (cm^{-1})): ν_{CO} 2107 (s), 2030 (s), 2018 (s), 2009 (m), 1952 (m), 1871 (s), 1827 (s). ^{1}H NMR (CDCl$_3$; δ (ppm)): 10.0 (m, 2H, $H_1H_{1'}$), 8.57 (d, 2H, $H_3H_{3'}$), 8.02 (s, 2H, $H_4H_{4'}$), 7.87 (dd, 2H, $H_2H_{2'}$). Visible spectrum (CHCl$_3$; λ_{max} (nm) (log ϵ)): 412 (3.63), 500 (3.43). Anal. Found (calcd) for $C_{18}H_8N_2O_6Cl_2WRu$: C, 30.8 (30.7); H, 1.18 (1.15); N, 4.08 (4.00).

[(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$] 4. To a solution of [Os(CO)$_3$Cl$_2$]$_2$ (93 mg, 0.135 mmol) in THF (5 mL) at 0−5 °C (ice bath) was added dropwise [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] (132 mg, 0.270 mmol) in THF (30 mL). After 1 h the temperature was raised to room temperature, and after 4 h the dark brown suspension was filtered off. The solution was evaporated to two-thirds of the original volume, and then, by adding *n*-hexane, compound **4** precipitated as a brown powder together with some amount of [(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$]·THF with one molecule of THF coordinated, as evidenced by the high number of carbonyl bands in the IR spectrum of the mixture (Table 1) and by its ^{1}H NMR spectum.[21] In CHCl$_3$ solution the mixture slowly rearranged to compound **4** (about 24 h), which was recovered by evaporation to dryness (yield 74%). IR (CHCl$_3$; (cm^{-1})): ν_{CO} 2107 (s), 2029 (vs), 2021 (s), 1951 (m), 1869 (m), 1827 (m). ^{1}H NMR (CDCl$_3$; δ (ppm)): 9.99 (m, 2H, $H_1H_{1'}$), 8.56 (d, 2H, $H_3H_{3'}$), 8.02 (s, 2H, $H_4H_{4'}$), 7.87 (dd, 2H, $H_2H_{2'}$), Visible spectrum (CHCl$_3$; λ_{max} (nm) (log ϵ)): 406 (3.66), 495 (3.39). Anal. Found (calcd) for $C_{18}H_8N_2O_6Cl_2WOs$: C, 27.5 (27.2); H, 1.06 (1.02); N, 3.56 (3.53).

Reactivity of 1 and 2 with PPh$_3$. To a solution of [(CO)$_3$(phen)W-*cis*-M(CO)$_2$Cl] (M = Rh(I) **1**, Ir(I) **2**; 0.08 mmol) in THF (10 mL) was added a solution of PPh$_3$ (43 mg, 0.16 mmol) in THF (10 mL) under a nitrogen atmosphere. The reaction is instantaneous, as confirmed by the IR spectrum registered after the addition of PPh$_3$, which shows the parallel formation of [W(CO)$_4$(phen)][9] and [*trans*-M(CO)Cl(PPh$_3$)$_2$] (M = Rh(I),[22b] Ir(I)[22a]) in quantitative yields.

Reactivity of 3 and 4 with PPh$_3$. To a solution of [(CO)$_3$(phen)W-*fac*-M(CO)$_3$Cl$_2$] (M = Ru(II) **3**, Os(II) **4**; 0.07 mmol)

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[21] For [(CO)$_3$(phen)W-*fac*-Ru(CO)$_3$Cl$_2$]·THF: ^{1}H NMR (CDCl$_3$; δ (ppm)) 9.62 (d, 2H, $H_1H_{1'}$), 8.48 (d, 2H, $H_3H_{3'}$), 8.01 (s, 2H, $H_4H_{4'}$), 7.79 (dd, 2H, $H_2H_{2'}$), 4.37 and 2.07 (two multiplets due to coordinated THF). For [(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$]·THF: ^{1}H NMR (CDCl$_3$; δ (ppm)) 9.63 (d, 2H, $H_1H_{1'}$), 8.48 (d, 2H, $H_3H_{3'}$), 8.01 (s, 2H, $H_4H_{4'}$), 7.79 (dd, 2H, $H_2H_{2'}$), 4.37 and 2.07 (two multiplets due to coordinated THF).

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in THF (10 mL) was added a solution of PPh_3 (37 mg, 0.14 mmol) in THF (10 mL) under a nitrogen atmosphere. The color turned slowly from brown to violet. When the reaction was followed by IR spectroscopy, after 5 h the complete transformation of compounds **3** and **4** into [W(CO)$_3$(phen)(PPh$_3$)][22c] and [*fac*-M(CO)$_3$Cl$_2$(PPh$_3$)] (M = Ru(II),[22d] Os(II)[22e]) was observed. The solution was evaporated to dryness, and the mixture was recrystallized from CHCl$_3$/*n*-hexane in order to separate the two products, the violet [W(CO)$_3$(phen)(PPh$_3$)] being insoluble in *n*-hexane and the white [*fac*-M(CO)$_3$Cl$_2$(PPh$_3$)] (M = Ru, Os) being soluble in *n*-hexane.

Reactivity of 1 with Pyridine. To a solution of compound **1** (50 mg, 0.078 mmol) in THF (20 mL), pyridine (6.5 mg, 0.080 mmol, 6.6 μL) was added under nitrogen atmosphere. Following the reaction by IR spectrum, after 2 h we observed the complete transformation of compound **1** into [W(CO)$_4$(phen)][9] and [*cis*-Rh(CO)$_2$Cl(py)].[23]

Reactivity of 3 and 4 with CO. Portions of compounds **3** and **4** (50 mg) were dissolved in THF (10 mL), and CO was bubbled through the solution. Following the reaction by IR spectroscopy, after 4 h we observed the complete conversion of compounds **3** and **4** into [W(CO)$_4$(phen)][9] and [*fac*-M(CO)$_3$Cl$_2$(THF)] (M = Ru(II), Os(II)).[24]

Attempted Synthesis of [(CO)$_3$(phen)WBF$_3$] 5. In a 50 mL flask equipped with a condenser, 43 mg of [*fac*-W(CO)$_3$(phen)(pyz)] were dissolved in 20 mL of CH$_2$Cl$_2$. To this violet solution was added dropwise BF$_3$·OEt$_2$ (10 μL). Immediately a green powder precipitated. It was filtered under nitrogen, washed with dry CH$_2$Cl$_2$ in order to remove a small amount of the adduct [pyzBF$_3$], and dried with a flux of dry nitrogen. The green powder was stored under nitrogen; after 2 h it became blue and insoluble in all common solvents (yield 70%). The freshly prepared material shows the following IR and analytical data. IR (Nujol; (cm^{-1})): ν_{CO} 2054 (vw), 2010 (s), 1924 (s); ν_{BF} 1087 (br). Anal. Found (calcd) for C$_{15}$H$_8$N$_2$O$_3$WBF$_3$·2CH$_2$Cl$_2$: C, 28.9 (29.8); H, 2.05 (1.75); N, 4.40 (4.08) These data suggest the loss of the pyrazine bridge and the presence of the W(CO)$_3$(phen) and BF$_3$ moieties.

Attempted Synthesis of [W(CO)$_3$(phen)-*cis*-Re(CO)$_4$Cl]. A 77 mg (0.115 mmol) portion of [Re(CO)$_4$Cl]$_2$ was dissolved in THF (10 mL) under a nitrogen atmosphere in order to obtain [*cis*-Re(CO)$_4$Cl(THF)]. To this solution, cooled in a ice bath, was slowly added a solution of [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] (112 mg, 0.229 mmol) in THF (30 mL). The mixture turned immediately black and then brown. At the end of the reaction we observed by IR spectroscopy the presence in solution of [W(CO)$_4$(phen)] and some [Re(CO)$_4$Cl]$_2$. This behavior suggests the probable formation of the very unstable bimetallic compound [W(CO)$_3$(phen)-*cis*-Re(CO)$_4$Cl], which rapidly decomposes to the very stable [W(CO)$_4$(phen)] and some [Re(CO)$_4$Cl]$_2$.

Attempted Synthesis of [W(CO)$_3$(phen)W(CO)$_5$]. To a solution of [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] (145 mg, 0.296 mmol) in THF (20 mL), cooled by an ice bath, was added dropwise a freshly prepared solution of [W(CO)$_5$(THF)][15] (117 mg, 0.296 mmol) in THF (16 mL) under a nitrogen atmosphere. After 4 h the brown solution was evaporated to a small volume and *n*-hexane was added. The precipitated brown powder was recognized as impure [W(CO)$_4$(phen)], while in the mother liquor the infrared spectrum suggested the presence of some [W(CO)$_6$] and [W(CO)$_5$(THF)].

X-ray Structure Determination of [(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] 2 and [(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$] 4. Suitable crystals of both compounds **2** and **4** were obtained by slow crystallization in CH$_2$Cl$_2$/*n*-hexane.

Crystal Data. Compound **2**: C$_{17}$H$_8$ClIrN$_2$O$_5$W, fw 731.75, orthorhombic, space group $P2_12_12$ (No. 18), $a = 17.337(4)$ Å, $b = 17.050(9)$ Å, $c = 6.905(8)$ Å, $Z = 4$, $d_{calcd} = 2.381$ Mg m^{-3}, $\mu = 123.0$ cm^{-1}, $F(000) = 1328$, $R = 0.048$, $R_w = 0.120$ for 1578 observed reflections ($I > 2\sigma(I)$). Compound **4**: C$_{18}$H$_8$Cl$_2$N$_2$O$_6$OsW, fw 793.23, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.3963(7)$ Å, $b = 11.3377(11)$ Å, $c = 12.3266(8)$ Å, $\alpha = 83.58(1)°$. $\beta = 88.50(1)°$, $\gamma = 82.00(1)°$, $Z = 2$, $d_{calcd} = 2.590$ Mg m^{-3}, $\mu = 121.92$ cm^{-1}, $F(000) = 724$, $R = 0.031$, $R_w = 0.075$ for 3785 observed reflections ($I > 2\sigma(I)$). Intensity data collection was performed with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer for compound **2** and on a Siemens SMART CCD diffractometer for compound **4**. Data sets were corrected for Lorentz–polarization effects, decay (only for **2**; maximum decay 6% at the end of the data collection), and absorption.[25] Both structures were solved by direct methods using SHELXS 86;[26] full-matrix least-squares refinements on F^2 were performed using SHELXL 93.[27] All non-H atoms were refined anisotropically, and H atoms were seen in difference Fourier maps, placed, and thereafter allowed to ride on their parent atoms. The significant structural parameters are reported in Table 2. Crystallographic data (excluding structure factors) for structures of compounds **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-213211 and 213212. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. code +(1223) 336-033; e-mail, teched@chemcrys.cam.ac.uk).

Voltammetric Investigation. The cyclic voltammetric investigation was carried out on carefully deareated CH$_2$Cl$_2$ solutions (typically 0.0008–0.001 M) with an Autolab PGSTAT 30 potentiostat/galvanostat run by a PC with GPES software. The solutions were made up with HPLC-grade CH$_2$Cl$_2$ and tetrabutylammonium perchlorate TBAP (>99% Fluka) as the 0.1 M supporting electrolyte. Each compound was studied in the interval −0.5 to +2.2 V (SCE), at different potential scan rates (v) ranging from 0.02 to 0.5 V s^{-1}, on an AMEL glassy-carbon-disk electrode (GC, ~2.5 mm diameter), using a platinum counter electrode and a saturated calomel electrode (SCE) as a reference. Since the reaction products appeared to strongly film the working electrode, the latter was carefully cleaned before each first cycle and the reproducibility of the resulting CV results carefully checked. The electrochemical reversibility and number of electrons transferred in the first oxidation peak for each compound were checked by classical tests such as E_p vs log v, $E_p - E_{p/2}$, and I_p vs $v^{1/2}$ analysis, plus deconvolution of the original CV characteristics followed by analysis of the resulting “stationary”, steplike waves in order to obtain the corresponding half-wave potentials $E_{1/2}$ and n (or αn) values.[28]

Results and Discussion

Synthesis of Bimetallic Complexes. The complex [*fac*-W(CO)$_3$(phen)(pyz)] was synthesized by reaction in THF at 0–5 °C of the known complex [*fac*-W(CO)$_3$(phen)(CH$_3$CN)][13] with a large excess of pyrazine (pyz) (1:10), in order to avoid the formation of the symmetrical dimer [(CO)$_3$(phen)W(pyz)W(phen)(CO)$_3$] which precipitates. The monomeric pyrazine compound which, according to its infrared spectrum in the carbonyl stretching region (Table 1), has a *fac* arrangement of the three

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[23] Heaton, B. T.; Jacob, C.; Sampanthar, J. T. *J. Chem. Soc., Dalton Trans.* **1998**, *8*, 1403.

[24] For Ru(CO)$_3$Cl$_2$(THF): ν_{CO} (THF) 2131 (s), 2056 (vs) cm^{-1}. For Os(CO)$_3$Cl$_2$(THF): ν_{CO} (THF) 2122 (s), 2034 (vs), 2025 (vs) cm^{-1}.

[25] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351. SADABS Area-Detector Absorption Correction Program, Bruker AXS, Inc. Madison, WI.

[26] Sheldrick, G. M. SHELXS 86. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[27] Sheldrick, G. M. SHELXS 93; University of Göttingen, Göttingen, Germany, 1993.

[28] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 2002; pp 231–239, 247–252.

carbonyl ligands as in the starting complex [*fac*-W(CO)$_3$(phen)(CH$_3$CN)], is slightly labile in solution toward pyrazine dissociation. In its ^{1}H NMR spectrum at room temperature in CDCl$_3$ or CD$_2$Cl$_2$ the slow formation of a certain amount of the symmetrical dimer [(CO)$_3$(phen)W(pyz)W(phen)(CO)$_3$] is detected. The latter separates slowly as an insoluble compound (see Experimental Section). The heteronuclear bimetallic complex **1** was first casually prepared in an attempt to synthesize heteronuclear bimetallic complexes, with pyrazine as bridging linker, by reaction of [*fac*-W(CO)$_3$(phen)(pyz)] with [Rh(CO)$_2$Cl]$_2$ in THF. The fragment W(CO)$_3$(phen) was still present in the reaction product, as suggested by IR and ^{1}H NMR spectra; however, both the elemental analysis and the ^{1}H NMR spectrum did not confirm the presence of the pyrazine bridge, suggesting the formation of a heteronuclear metal−metal bond, as confirmed later by the X-ray structural determination of the related iridium compound **2** (see later), with a W−Ir heteronuclear early−late metal−metal bond. (Figure 1). By reaction of [*fac*-W(CO)$_3$(phen)(pyz)] with BF$_3$(OEt$_2$) in CH$_2$Cl$_2$, a green powder separated **5**, very insoluble in all common solvents and unstable even under a nitrogen atmosphere (in 2 h the color turns from green to blue). Due to its instability it was not possible to characterize **5** in a satisfactory way by elemental analyses. However, both ν_{CO} and ν_{BF} stretchings of its solid-state IR spectrum (Table 1) and the order of magnitude of the elemental analyses suggest the loss of the pyrazine bridge and the presence of both *fac*-W(CO)$_3$(phen) and BF$_3$ moieties.

The tendency of the W(CO)$_3$(phen) fragment to behave as a σ-donor base toward various “soft” organometallic acceptors was successfully confirmed, using as starting material the more easily available complex [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] according to the reactions

$$[\mathit{fac}\text{-W(CO)}_3\text{(phen)(CH}_3\text{CN)}] + {}^1/_2[\text{Rh(CO)}_2\text{Cl}]_2 \xrightarrow{\text{THF}} \underset{\mathbf{1}}{[\text{(CO)}_3\text{(phen)W-}\mathit{cis}\text{-Rh(CO)}_2\text{Cl}]} + \text{CH}_3\text{CN} \quad (2)$$

$$[\mathit{fac}\text{-W(CO)}_3\text{(phen)(CH}_3\text{CN)}] + [\mathit{cis}\text{-Ir(CO)}_2\text{Cl(pyz)}] \xrightarrow{\text{THF}} \underset{\mathbf{2}}{[\text{(CO)}_3\text{(phen)W-}\mathit{cis}\text{-Ir(CO)}_2\text{Cl}]} + \text{CH}_3\text{CN} + \text{pyz} \quad (3)$$

$$[\mathit{fac}\text{-W(CO)}_3\text{(phen)(CH}_3\text{CN)}] + {}^1/_2[\mathit{fac}\text{-M(CO)}_3\text{Cl}_2]_2 \xrightarrow{\text{THF}} [\text{(CO)}_3\text{(phen)W-}\mathit{fac}\text{-M(CO)}_3\text{Cl}_2] + \text{CH}_3\text{CN} \quad (4)$$
$$\text{M} = \text{Ru } \mathbf{3}, \text{Os } \mathbf{4}$$

Infrared spectra (Table 1) suggest for compounds **1** and **2** a *cis* geometry of the two carbonyl ligands and for compounds **3** and **4** three carbonyl ligands with a *fac* geometry. These suggestions were confirmed by the X-ray structural determinations of **2** and **4** (Figures 1 and 2, respectively). Although compounds **3** and **4** were the major components of the reaction mixtures, small amounts of the *fac* isomer with one THF molecule coordinated to one of the two metal atoms were obtained in parallel, as evidenced by the IR and ^{1}H NMR spectra of the reaction mixtures (see Experimental Section). We were unable to isolate with an acceptable purity the adducts [(CO)$_3$(phen)W-*fac*-M(CO)$_3$Cl$_2$]·THF (M = Ru, Os); however, the presence of coordinated THF was evidenced by the ^{1}H NMR spectra in CDCl$_3$ with the THF signal shifted downfield by about 0.5 ppm with respect to THF as such. In CHCl$_3$ solution these mixtures slowly rearrange only to compounds **3** and **4**, respectively. An attempt to synthesize the complex [(CO)$_3$(phen)W-*cis*-Re(CO)$_4$Cl] by dropping a solution of [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] in THF into a solution of [*cis*-Re(CO)$_4$Cl(THF)] in THF at 0−5 °C failed. The solution turned immediately dark brown with the formation of an unstable species, probably the expected bimetallic complex, which quickly decomposes into [W(CO)$_4$(phen)], easily separated and purified, and a brown precipitate, probably an insoluble carbonyl cluster of rhenium which we were unable to characterize. A similar reaction occurred when we tried to synthesize the complex [(CO)$_3$(phen)W−W(CO)$_5$] by reaction in THF of [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] at 0−5 °C with [W(CO)$_5$(THF)]. A brown solution, probably the expected

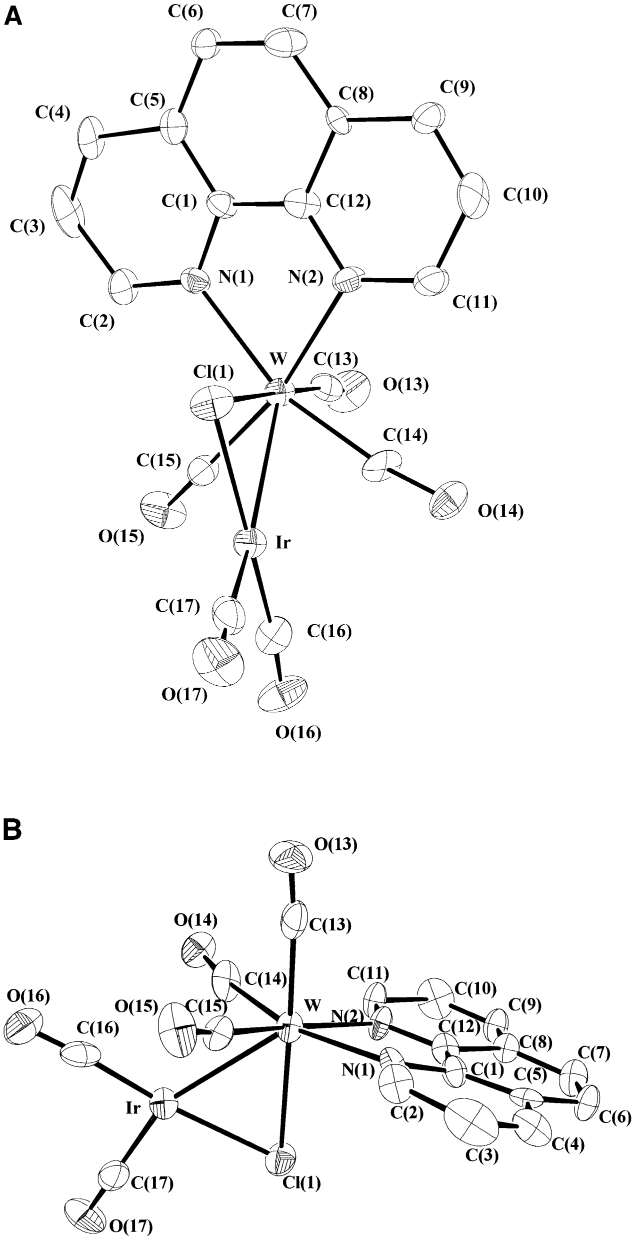

Figure 1. Two perspective views of [(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] **2**.

Table 1. IR Carbonyl Stretchings

compd	ν_{CO} (cm^{-1})	solvent
$[W(CO)_3(phen)(CH_3CN)]$[12]	1898 (vs), 1783 (s)	CH_3CN
$[W(CO)_3(phen)(pyz)]$	1898 (s), 1786 (br)	CH_2Cl_2
	1883 (s), 1785 (s), 1758 (vs)	Nujol
[*cis*-$Rh(CO)_2Cl(pyz)$][13]	2092 (s), 2019 (s)	CH_2Cl_2
	2086 (s), 2012 (s)	THF
[*cis*-$Ir(CO)_2Cl(pyz)$][13]	2081 (s), 2001 (s)	CH_3CN
	2081 (s), 2008 (s)	CH_2Cl_2
[*fac*-$Ru(CO)_3Cl_2(pyz)$][13]	2139 (s), 2079 (s), 2055 (s)	CH_2Cl_2
[*fac*-$Os(CO)_3Cl_2(pyz)$][13]	2131 (s), 2057 (s), 2029 (s)	CH_2Cl_2
$[(CO)_3(phen)W$-*cis*-$Rh(CO)_2Cl]$ **1**	2063 (s), 1997 (s), 1929 (s), 1834 (s)	$CHCl_3$
$[(CO)_3(phen)W$-*cis*-$Ir(CO)_2Cl]$ **2**	2054 (s), 1980 (s), 1938 (m), 1840 (br)	CH_2Cl_2
$[(CO)_3(phen)W$-*fac*-$Ru(CO)_3Cl_2]$ **3**	2107 (s), 2030 (s), 2018 (s), 1952 (m), 1871 (s), 1827 (s)	$CHCl_3$
$[(CO)_3(phen)W$-*fac*-$Ru(CO)_3Cl_2]\cdot$THF	2124 (m), 2024 (vs), 2005 (s), 1950 (s), 1888 (vs), 1838 (s)	THF
$[(CO)_3(phen)W$-*fac*-$Os(CO)_3Cl_2]$ **4**	2107 (s), 2029 (vs), 2021 (s), 1951 (s), 1869 (m), 1827 (m)	$CHCl_3$
$[(CO)_3(phen)W$-*fac*-$Os(CO)_3Cl_2]\cdot$THF	2125 (m), 2025 (vs), 2006 (s), 1949 (s), 1888 (s), 1838 (s)	THF
$[(CO)_3(phen)WBF_3]$ **5**	2054 (vw), 2010 (s), 1924 (s)	Nujol

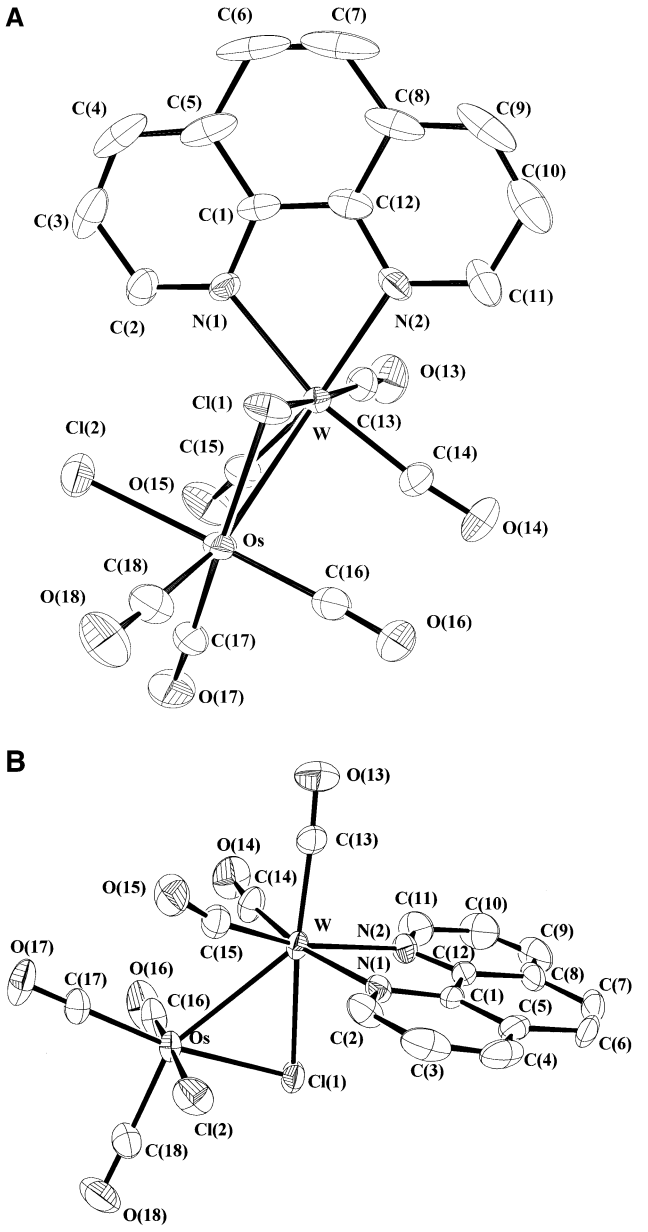

Figure 2. Two perspective views of $[(CO)_3(phen)W$-*fac*-$Os(CO)_3Cl_2]$ **4**.

bimetallic compound, was suddenly formed, which was very unstable, decomposing quickly with formation of $[W(CO)_4(phen)]$ and some $[W(CO)_6]$. It appears thus that when the two fragments have similar electronic properties such as W(0) and Re(I) (both 5d^6) or two W(0) species, an easy breakup of the metal–metal bond takes place with the shift of a carbonyl ligand.

IR and ^{1}H NMR Spectra. In the IR spectra (Table 1) of complexes **1**–**4** the stretchings of the carbonyls of the fragment $W(CO)_3(phen)$ are at higher frequencies (about 50 cm^{-1}) with respect to [*fac*-$W(CO)_3(phen)(CH_3CN)$] or [*fac*-$W(CO)_3(phen)(pyz)$], as expected for a W atom acting as a σ-donor base. At the same time the stretchings of the carbonyls of the Rh(I), Ir(I), Ru(II), and Os(II) acceptor fragments are shifted to slightly lower frequencies with respect to Rh(I) or Ir(I) *cis* or Ru(II) or Os(II) *fac* carbonyl complexes with a rather weak σ-donor base such as pyrazine[14] (Table 1). These observations suggest a not irrelevant σ donation from the W atom. The IR spectrum in Nujol of **5** shows the three stretching carbonyl bands expected for the $W(CO)_3(phen)$ fragment but at much higher frequencies ($\Delta\nu \approx$ 150 cm^{-1}) with respect to the complex [*fac*-$W(CO)_3(phen)(pyz)$] together with the band between 1000 and 1100 cm^{-1} attributable to the stretching ν_{B-F} of a BF_3 group (Table 1).

The IR spectra in $CHCl_3$ of complexes **3** and **4** show six carbonyl bands, of which three bands, at lower frequency, are attributable to ν_{CO} stretching of a *fac*-$W(CO)_3(phen)$ fragment; the other three, at high frequency, are due to the ν_{CO} stretching of the fragment *fac*-$M(CO)_3Cl_2$ (M = Ru, Os). If a molecule of THF is coordinated to compounds **3** and **4**, the stretchings of some carbonyl bands are slightly shifted, about 10–20 cm^{-1} to higher frequency (Table 1).

The ^{1}H NMR spectra of complexes **1**–**4** in $CDCl_3$ are very similar. They are characterized by a slight downfield shift, with respect to free phenanthroline, of the protons in the positions α to the coordinated nitrogen atoms. This shift is due to the electron transfer from the phenanthroline ligand to W.[29] In addition, the ^{1}H NMR spectra suggest a perfect symmetry of the phenanthroline ligand along the axis W–M, as later confirmed by the X-ray structure of compounds **2** (Figure 1) and **4** (Figure 2). The ^{1}H NMR spectra also show that the acceptor properties of the fragments *fac*-$M(CO)_3Cl_2$ (M = Ru,Os) are slightly higher than that of *cis*-$M(CO)_2Cl$ (M = Rh, Ir), since the protons of the phenanthroline ligand in the positions α to the nitrogen atoms are more

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[29] Roberto, D.; Ugo, R.; Tessore, F.; Lucenti, E.; Quici, S.; Vezza, S.; Fantucci, P.; Invernizzi, I.; Bruni, S.; Ledoux-Rak, I.; Zyss, J. *Organometallics* **2002**, *21*, 161.

shifted to low field in complexes containing Ru(II) and Os(II) (Δδ about 0.5 ppm) than in those containing Rh(I) and Ir(I) (Δδ about 0.3 ppm). Finally, when THF is coordinated to compounds **3** and **4**, this shift to low field is intermediate (Δδ about 0.4 ppm), with a parallel shift downfield of about 0.5 ppm of the THF signal, so that in the ^{1}H NMR spectrum the simultaneous presence of some [(CO)$_3$(phen)W-*fac*-M(CO)$_3$Cl$_2$]·THF (M = Ru, Os) adducts is easily identified.[21]

X-ray Structures of [(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] and [(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$]. Perspective views of the structure of [(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] **2** and [(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$] **4** are shown in Figures 1 and 2, respectively; selected interatomic distances and angles are reported in Table 2. Both structures confirm the coordination of a W(CO)$_3$(phen) moiety to a *cis*-Ir(CO)$_2$Cl and a *fac*-Os(CO)$_3$Cl$_2$ fragment formally by a kind of acid−base interaction, with the W atom acting as a σ-donor base. In both complexes this interaction gives rise to a W−M bond asymmetrically bridged by a chlorine atom; the W−M bond length (2.728(2) Å for M = Ir and 2.958(1) Å for M = Os) falls in the range of values usually reported for single bonds.[30] The symmetry of the X-ray structures of **2** and **4** is what is expected on the basis of the ^{1}H NMR spectra. The tungsten atom achieves a distorted (6 + 1) octahedral coordination, with the two nitrogen atoms of the phenanthroline ligand and two carbonyls defining the equatorial plane of the octahedron, whereas a chlorine ligand and the remaining carbonyl are located in apical positions. The arrangement of the carbonyl ligands in the W(CO)$_3$(phen) fragment is in agreement with the *fac* geometry suggested by the IR spectra. Significant deviations from the idealized octahedral geometry are evident. For instance, the departure of the N(1)−W−N(2) angle from the ideal 90° value (73.6(7) and 73.6(2)°, in **2** and **4**, respectively) is determined by the bite of the phenanthroline ligand. The C(13)−W−C(14) and C(13)−W−C(15) angles are also quite lower than 90°, but the C(14)−W−C(15) angle is significantly enlarged. The M atom (M = Ir, Os) can also be envisioned as almost capping a triangular face of the octahedron, defined by the atoms Cl(1), C(14), and C(15). Short contacts with carbonyls 14 and 15 are observed for complex **2** (Ir···C(14) = 2.62(3) Å, Ir···C(15) = 2.69(3) Å), which however are ca. 0.5 Å larger than typical Ir−CO (bridging or semibridging) distances. In complex **4** the Os atom, upon formation of a single W−Os bond, achieves a distorted-octahedral coordination. Here again a relatively short contact of 2.747(7) Å between Os and carbonyl CO(15) is observed. These weak interactions observed in either **2** or **4** do not produce large deviations from linearity of the W−C−O system involved, but only a pushing of the CO(14) and CO(15) ligands out of the equatorial plane of the octahedron toward CO(13), and thus account for the distortions observed. The Ir−Cl(1) distance found in **2** (2.368(7) Å) is much closer to typical Ir−Cl(terminal) distances rather than to Ir−Cl(bridging) distances.[31] The same holds for the Os−Cl(1) distance in **4**, which is even slightly shorter than a typical terminal Os−Cl distance.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] 2 and [(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$] 4

	M = Ir **2**	M = Os **4**
M−W	2.728(2)	2.958(1)
M−Cl(1)	2.368(7)	2.399(2)
M−Cl(2)		2.418(2)
M−C(16)	1.76(3)	1.895(8)
M−C(17)	1.86(3)	1.896(7)
M−C(18)		1.927(8)
W−Cl(1)	2.567(8)	2.540(2)
W−N(1)	2.22(2)	2.242(5)
W−N(2)	2.20(2)	2.221(5)
W−C(13)	1.98(3)	1.956(7)
W−C(14)	1.97(2)	1.942(7)
W−C(15)	1.97(3)	1.967(7)
C(13)−O(13)	1.16(4)	1.149(9)
C(14)−O(14)	1.16(3)	1.153(8)
C(15)−O(15)	1.14(3)	1.159(9)
C(16)−O(16)	1.12(4)	1.118(11)
C(17)−O(17)	1.12(4)	1.115(9)
C(18)−O(18)		1.119(10)
N(1)−C(1)	1.38(3)	1.382(8)
N(1)−C(2)	1.32(3)	1.329(8)
N(2)−C(11)	1.33(4)	1.353(10)
N(2)−C(12)	1.37(3)	1.376(9)
C(1)−C(5)	1.43 (4)	1.401(10)
C(1)−C(12)	1.37 (3)	1.418(9)
C(2)−C(3)	1.49 (5)	1.395(11)
C(3)−C(4)	1.32 (5)	1.338(15)
C(4)−C(5)	1.45(4)	1.408(13)
C(5)−C(6)	1.47(4)	1.444(15)
C(6)−C(7)	1.31 (4)	1.319(16)
C(7)−C(8)	1.43 (4)	1.427(17)
C(8)−C(9)	1.45 (4)	1.382(14)
C(8)−C(12)	1.43(3)	1.406(10)
C(9)−C(10)	1.34 (5)	1.325(18)
C(10)−C(11)	1.48(4)	1.366(12)
N(1)−W−N(2)	73.6(7)	73.6(2)
N(1)−W−C(15)	94.0(9)	93.9(2)
N(2)−W−C(14)	91.0(9)	94.6(3)
N(1)−W−C(14)	162.9(9)	167.9(2)
N(2)−W−C(15)	167.5(9)	160.1(2)
N(1)−W−Cl(1)	86.2(6)	82.8(1)
N(2)−W−Cl(1)	83.1(6)	83.8(2)
N(1)−W−C(13)	94(1)	96.8(2)
N(2)−W−C(13)	98(1)	89.4(2)
C(13)−W− C(14)	80(1)	79.6(3)
C(13)−W− C(15)	81(1)	76.5(3)
C(14)−W− C(15)	101(1)	96.5(3)
Cl(1)−W−M	53.0(2)	51.05(4)
Cl(1)−W−C(13)	179(1)	173.0(2)
Cl(1)−W−C(14)	99.6(8)	99.4(2)
Cl(1)−W−C(15)	98.6(8)	110.5(2)
Cl(1) −M−W	60.0(2)	55.42(4)
Cl(1)−M−C(17)	96(1)	169.9(2)
C(16)−M−C(17)	92(1)	91.3(3)
C(16)−M−W	113(1)	91.0(2)
Cl(1)−M−C(16)	172(1)	90.3(2)
W−M−C(17)	155(1)	114.6(2)
M−Cl(1)−W	66.9(2)	73.53(5)
Cl(1)−M−C(17)		169.9(2)
Cl(1)−M−C(18)		97.9(2)
C(17)−M−C(18)		92.0(3)
C(18)−M−W		153.1(2)
Cl(2)−M−C(16)		176.7(2)
Cl(2)−M−C(17)		90.0(2)
Cl(2)−M−C(18)		84.2(3)
Cl(2)−M−W		91.17(5)
Cl(2)−M−Cl(1)		88.93(7)
C(16)−M−C(18)		92.8(3)

Reactivity toward PPh$_3$, Pyridine, and CO and an Investigation of Oxidative Additions on Rh(I) and Ir(I) Centers. The direct linking of two electroni-

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cally different transition-metal atoms usually produces a heteronuclear complex with a polar metal−metal bond. The polarity is influenced not only by the nature of the metals involved but also by the set of ligands coordinated to the metals. The greater the disparity of the electronic properties of the linked metallorganic fragments, the greater the polarity of the metal−metal bond. This concept is realized in its extreme form in the chemistry of *early-late* heteronuclear bimetallic complexes, whose study was initially hampered by the apparent instability of most compounds synthesized. However, the early−late heteronuclear bimetallic complexes **1**−**4** synthesized in this work, which cannot be considered classical in the sense of Gade's definition,[32] are very stable in the solid state and in solution, suggesting a heteronuclear metal−metal bond relatively inert with respect to an electron-transfer process such as homolytic or heterolytic cleavage. This stability suggests thus that the W−M bond in compounds **1**−**4** cannot be described by a total sharing of bonding electrons,[32] but better by a reversible σ donation from the W atom, without a real change of the oxidation state of the donor and acceptor centers. The formation of heteronuclear bimetallic complexes where the basic metal may act as a donor to donate electrons to another metal with formation of a donor−acceptor bond has been well described.[33] To confirm this picture, we investigated the σ-donor properties of the W(CO)$_3$(phen) fragment by ligand displacement reactions with relatively weak σ-donor ligands with increasing π-acceptor properties such as CO > PPh$_3$ > pyridine.

Reactions with PPh$_3$ were carried out in THF by adding a solution of PPh$_3$ to a solution of the bimetallic complex in the molar ratio 2:1. The replacement of W(CO)$_3$(phen) is immediate for complexes **1** and **2**, with breaking of the metal−metal bond and the simultaneous shift of a carbonyl ligand according to

$$[(\mathrm{CO})_3(\mathrm{phen})\mathrm{W}\text{-}cis\text{-}\mathrm{M}(\mathrm{CO})_2\mathrm{Cl}] + 2\mathrm{PPh}_3 \rightarrow [trans\text{-}\mathrm{M}(\mathrm{CO})\mathrm{Cl}(\mathrm{PPh}_3)_2] + [\mathrm{W}(\mathrm{CO})_4(\mathrm{phen})] \quad (5)$$

$$\mathrm{M} = \mathrm{Rh(I)},^{22a}\ \mathrm{Ir(I)}^{22b}$$

while with compounds **3** and **4** the same reaction is slower (5 h) so that it can be followed easily by the disappearance of the band at 1950 cm^{-1} in the IR spectrum (Table 1), characteristic of the presence of the metal−metal bond. Two compounds are formed, in accordance with reaction (6), easily separated by crystallization (CHCl$_3$/*n*-hexane), the violet W[22c] compound being insoluble in *n*-hexane and the white Ru and Os compounds[22d,e] being soluble in *n*-hexane:

$$[(\mathrm{CO})_3(\mathrm{phen})\mathrm{W}\text{-}fac\text{-}\mathrm{M}(\mathrm{CO})_3\mathrm{Cl}_2] + 2\mathrm{PPh}_3 \rightarrow \underset{\text{violet}}{[fac\text{-}\mathrm{W}(\mathrm{CO})_3(\mathrm{phen})(\mathrm{PPh}_3)]} + \underset{\text{white}}{[fac\text{-}\mathrm{M}(\mathrm{CO})_3\mathrm{Cl}_2(\mathrm{PPh}_3)]} \quad (6)$$

$$\mathrm{M} = \mathrm{Ru(II)},^{22d}\ \mathrm{Os(II)}^{22e}$$

This reactivity suggests that PPh$_3$ behaves as a ligand softer than W(CO)$_3$(phen) toward M(I) (M = Rh, Ir) and M(II) (M = Ru, Os) soft carbonyl complexes.

Table 3. Absorption (λ_a) and Emission (λ_e) Electronic Spectra in CHCl$_3$

compd	λ_a (nm)	λ_e (nm)[a]
[W(CO)$_4$(phen)][8,12]	388 (3.41), 499 (3.79)[b]	568[c]
[W(CO)$_3$(phen)(CH$_3$CN)][12]	350 (sh), 526 (3.4)[b,d]	*e*
[W(CO)$_3$(phen)(pyz)]	356 (2.87), 511 (3.09),[f] 578 (3.28)[b,c]	*e*
[(CO)$_3$(phen)W-*cis*-Rh(CO)$_2$Cl][g] **1**	392 (3.86), 444 (3.65),[h] 517 (3.85)[b]	506, 595
[(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] **2**	385 (3.74),[h] 503 (3.59)[b]	622
[(CO)$_3$(phen)W-*fac*-Ru(CO)$_3$Cl$_2$] **3**	412 (3.63),[h] 500 (3.43)[b]	552
[(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$] **4**	406 (3.66),[h] 495 (3.39)[b]	567

[a] Exciting wavelength $\lambda = \lambda_{\max}$ of MLCT. [b] Attributed to a MLCT (W → π^*_{phen}). [c] In CH$_2$Cl$_2$. [d] In CH$_3$CN. [e] Not fluorescent. [f] Attributed to MLCT (W→π^*_{pyz}). [g] The assignment of the bands was determined by deconvolution. [h] Attributed to an additional MLCT transition (M → π^*_{phen}).

A similar substitution takes place by reaction in THF of the complex [(CO)$_3$(phen)W-*cis*-Rh(CO)$_2$Cl] **1** with the less soft pyridine (py) ligand. The reaction is complete in 2 h with formation of [W(CO)$_4$(phen)] and [*cis*-Rh(CO)$_2$Cl(py)].[23] Therefore, also a less soft, better σ-donor and lower π-acceptor with respect to PPh$_3$ such as pyridine still behaves as a softer ligand than W(CO)$_3$(phen). Thus, it was not surprising that by reaction of the much softer ligand CO with complexes **3** and **4**, an easy substitution reaction takes place according to

$$[(\mathrm{CO})_3(\mathrm{phen})\mathrm{W}\text{-}fac\text{-}\mathrm{M}(\mathrm{CO})_3\mathrm{Cl}_2] + \mathrm{CO} \xrightarrow{\mathrm{THF}} [\mathrm{W}(\mathrm{CO})_4(\mathrm{phen})] + [fac\text{-}\mathrm{M}(\mathrm{CO})_3\mathrm{Cl}_2(\mathrm{THF})] \quad (7)$$

$$\mathrm{M} = \mathrm{Ru(II)},^{24}\ \mathrm{Os(II)}^{24}$$

The relatively poor soft properties of W(CO)$_3$(phen) as a ligand were confirmed by the complete inertness of the bimetallic Rh(I) and Ir(I) complexes **1** and **2** toward oxidative reactions not only with H$_2$ but also with the rather reactive CH$_3$I, which reacts easily with Rh(I) and Ir(I) complexes with a very soft ligand environment such as [*trans*-Ir(PPh$_3$)$_2$(CO)Cl] or [Rh(CO)$_2$I$_2$]$^-$.[34]

When the interaction occurs with a hard σ−δonor ligand such as an excess of THF, complexes **1** and **2** are very stable; only for complexes **3** and **4** do we have evidence of a coordinative interaction of one THF molecule, but without breaking of the metal−metal bond. This interaction may involve the breaking of the weak chlorine bond with the W center due to the bridging chlorine by a weak interaction with a THF molecule, which therefore is probably located in the coordination sphere of the W atom.

Electronic Spectra and Voltammetric Investigation. The visibile spectrum in CHCl$_3$ solution of [W(CO)$_4$(phen)] (Table 3) shows a metal to ligand transition MLCT (W → π^*_{phen}) at 499 nm, together with ligand field LF (d → d) transitions at higher energy.[9,13] Electron-acceptor substituents, such as the nitro group, on the phenanthroline ligand lower the energy of this MLCT transition.[9,13] A significant shift to lower energy is shown also by substitution of a CO ligand by a better σ-donor ligand, as in [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] (526 nm in CH$_3$CN), if compared to [W(CO)$_4$(phen)] (451 nm

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Table 4. Dependence of the λ_{max} (nm) Values of the MLCT Transitions on the Solvent Polarity

compd	transition	λ_{max}								
		toluene	$CHCl_3$	ethyl acetate	THF	CH_2Cl_2	CH_3CN	dichloroethane	acetone	DMF
[(CO)$_3$(phen)W-*cis*-Rh(CO)$_2$Cl] **1**	*a*	448	444		432	434		433	424	
	MLCT	528	517		500	503		491	469	
[(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] **2**	*a*	384	385		380	380			371	
	MLCT	515	503		489	488			461	
[(CO)$_3$(phen)W-*fac*-Ru(CO)$_3$Cl$_2$] **3**	*a*	414	412	398	401	396	385	397	389	388
	MLCT	514	500	488	491	484	458	482	469	462
[(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$] **4**	*a*	415	406		402	399				387
	MLCT	508	495		484	475				465

[a] Attributed to an additional MLCT ($M \rightarrow \pi^*_{phen}$).

Table 5. CV Peak Potentials, E_p(I,ox), and Half-Wave Potentials (after Deconvolution), $E_{1/2}$, for the First Oxidation Step of Different Metal Complexes[a]

compd	E_p(I ,ox)/ V (SCE)	$E_{1/2}$/ V (SCE)	remarks
[W(CO)$_4$(phen)]	0.765	0.733	1e; approaching EC reversibility at low scan rates; no return peak
[W(CO)$_4$(phen)(CH$_3$CN)]	0.219	0.196	1e; approaching EC reversibility at low scan rates; return peak
[(CO)$_3$(phen)W-*cis*-Rh(CO)$_2$Cl] **1**	0.785	0.715	1e; irreversible peak; second oxidation peak at 1.2 V
[(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$] **4**	0.921	0.893	1e; EC reversible peak with return peak
[*fac*-Os(CO)$_3$Cl(pyz)]			no peaks in the investigated range
[*cis*-Rh(CO)$_2$Cl(pyz)]	1.46		flat, shoulder-like signal

[a] Conditions: CH_2Cl_2 + 0.1 M TBAP medium; glassy-carbon electrode, scan rate 0.2 V s^{-1}.

in CH_3CN), or as in [*fac*-W(CO)$_3$(phen)(pyz)] (578 nm in CH_2Cl_2), if compared to [W(CO)$_4$(phen)] (482 nm in CH_2Cl_2). These two kinds of shifts have different origins. While substitution on the phenanthroline ligand by a nitro group induces a stabilization of the acceptor π^*_{phen} orbitals, the substitution of one π-acceptor carbonyl ligand by a better σ-donor ligand such as CH_3CN or pyrazine produces probably a shift to slightly higher energy of the occupied d orbitals of the W(0) atom. As we will see later, this hypothesis has been confirmed by a voltammetric investigation.

The visible spectra in $CHCl_3$ solution of the heteronuclear bimetallic complexes **1**−**4** show two bands in the region 385−517 nm, both solvatochromic and both of comparable intensity (log ϵ about 3.5) (Table 3). The band at lower energy can be attributed to the well-described MLCT transition ($W \rightarrow \pi^*_{phen}$) of the W(CO)$_3$(phen) fragment, only slightly red-shifted with respect to [W(CO)$_4$(phen)]. The attribution of the second band at higher energy is not straightforward. Its significant solvatochromism (Table 4) excludes an assignment to the poorly solvatochromic $\pi \rightarrow \pi^*$ transitions of the phenanthroline ligand of the W(CO)$_3$(phen) moiety, and its absence in the electronic spectra of the monomeric complexes [W(CO)$_4$(phen)], [*fac*-W(CO)$_3$(phen)(CH$_3$CN)], and [*fac*-W(CO)$_3$(phen)(pyz)] (Table 3) confirms that its origin is due to the presence of the metal−metal bond. Its significant solvatochromism would suggest either an additional $W \rightarrow \pi^*_L$ MLCT transition or a metal to metal charge transfer (MMCT).

It is reported that the complex [W(CO)$_4$(phen)] should have, in addition to the three allowed MLCT transitions, within the absorption band at 499 nm involving the first π^*_{phen} level, two allowed MLCT transitions at higher energies involving the second π^*_{phen} level.[35] Not only will the formation of the bimetallic species alter the overall symmetry properties but also the metal−metal bond will clearly affect the energies of the d orbitals of the W(0) atom. Therefore, in complexes **1**−**4** the MLCT transitions $W \rightarrow \pi^*_{phen}$ involving the second π^*_{phen} level could be shifted to lower energy at about 400 nm. This assignment is supported by the significant blue-shifted solvatochromism (corresponding to a decrease of the dipole moment in the excited state typical of a $W \rightarrow \pi^*_{phen}$ transition) and by the intensity of the band at about 400 nm (Table 3). The attribution to a MMCT would require in the excitation process an electron transfer from the oxidized metal centers (M = Rh(I), Ir(I), Ru(II), Os(II)) to the W(0) atom in order to justify the blue-shifted solvatochromism. MMCT transitions were reported for complexes with a heteronuclear metal−metal bond, with the Fe(0) atom of [*trans*-Fe(CO)$_3$L$_2$] (L is a particular tertiary phosphine) acting as a σ donor toward a series of Lewis acids.[33] However, the attribution of absorption bands of quite variable intensity to a MMCT process was based only on the agreement of their energy with Jørgensen's theory of charge-transfer transitions, and in any case the electron-transfer process was proposed to take place from the Fe(0) atom to the second acceptor metal atom.

The voltammetric behavior of [W(CO)$_4$(phen)], [*fac*-W(CO)$_3$(phen)(CH$_3$CN)], and complexes **1** and **4**, when compared to that of [*cis*-Rh(CO)$_2$Cl(pyz)] and [*fac*-Os(CO)$_3$Cl$_2$(pyz)] (Table 5), shows that the W(0) atom is always easily oxidized, the oxidability decreasing on going from [*fac*-W(CO)$_3$(phen)(CH$_3$CN)] to [W(CO)$_4$(phen)] and finally to **1** and **4**, respectively, as expected for a decrease of the electron density on the W(0) atom due to an increased electron donation. However, the Os(II) atom is not oxidized either in [*fac*-Os(CO)$_3$Cl$_2$(pyz)] or in **4**, while the Rh(I) atom is oxidized, but much less easily than the W(0) atom, either in [*cis*-Rh(CO)$_2$Cl(pyz)] or in **1** (Table 5). This trend would suggest that the d electron density located on the oxidized acceptor centers (either Rh(I) or Os(II)) is not easily available for an electron-transfer process, differently from the d electron

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(35) Servaas, P. C.; van Dijk, H. K.; Snoeck, T. L.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 4494.

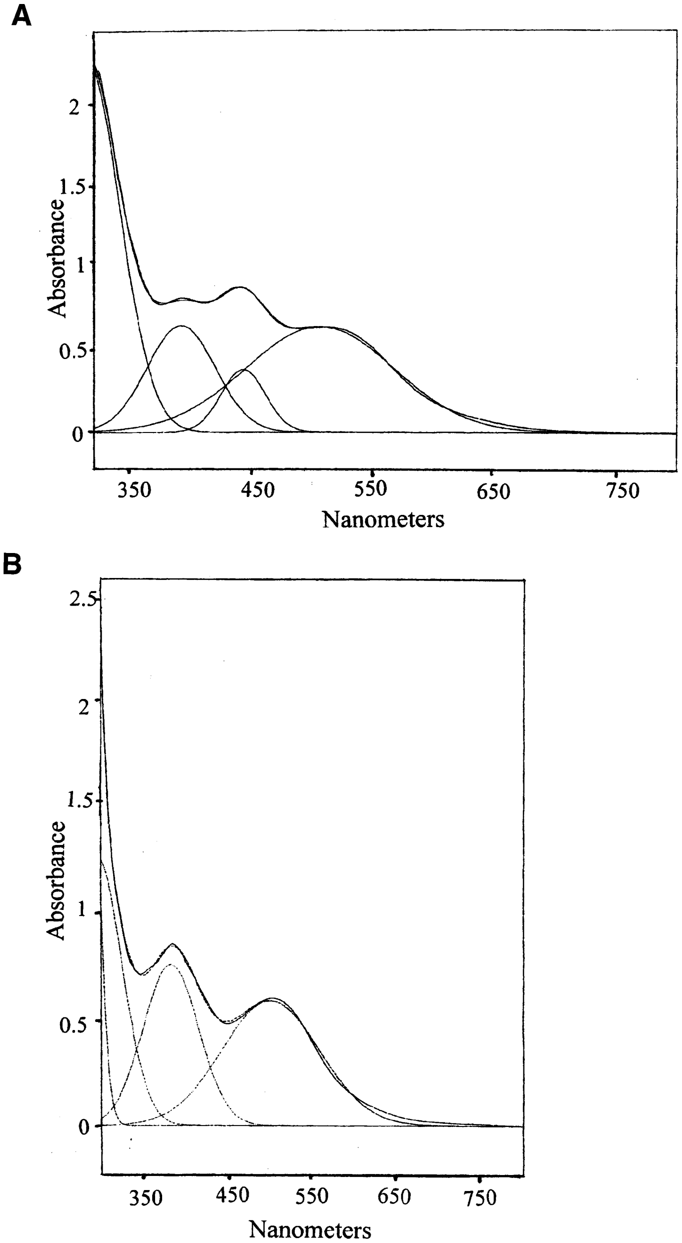

Figure 3. Absorption electronic spectra in $CHCl_3$ of (a, top) $[(CO)_3(phen)W\text{-}cis\text{-}Rh(CO)_2Cl]$ **1** and (b, bottom) $[(CO)_3(phen)W\text{-}cis\text{-}Ir(CO)_2Cl]$ **2** by deconvolution.

density located on the W(0) atom. As a consequence, the attribution of the relatively strong absorption bands around 400 nm to a MMCT process with electron transfer from the oxidized metal centers to the W(0) atom, in agreement with the blue-shifted solvatochromism, is not substantiated.

One major difference must be stressed between the spectra of **1** and **2** in the region 370−450 nm (Figure 3). While **1** shows a solvatochromic band at 444 nm together with a stronger, but much less solvatochromic, band at 392 nm, **2** shows only a solvatochromic band at 385 nm (Table 3 and Figure 3). Attempts to detect for the complex **2** by deconvolution an absorption band in the region 420−450 nm covered by the strong absorption at 385 nm failed.

Complexes **1**−**4** all show an emission when irradiated at the lower energy MLCT wavelength (Table 3). The emission bands are always solvatochromic, having a blue shift with increasing polarity of the solvent. However, we did not obtain the expected linear relationship of the solvatochromic shift of the emission bands with the solvent polarity, required in order to use both the absorption and the emissive solvatochromic data for the determination of the solvent cavity radius *a* (Table 6).[19]

EFISH and Solvatochromic Investigation of the Second-Order NLO Response of Heteronuclear Bimetallic Complexes. The molecular quadratic hyperpolarizability β_λ at the incident wavelength λ of bimetallic complexes **1**−**4** was measured in $CHCl_3$ solution using the EFISH tecnique,[17] which provides information through the equation

$$\gamma_{\mathrm{EFISH}} = (\mu\beta_\lambda/5kT) + \gamma(-2\omega;\,\omega,\,\omega,\,0) \qquad (8)$$

where $\mu\beta_\lambda/5kT$ is the dipolar orientational contribution and $\gamma(-2\omega;\,\omega,\,\omega,\,0)$, a third-order term at frequency ω of the incident radiation, is the electronic contribution always considered negligible in these kinds of metal complexes.[5,8] β_λ (or $\beta_{1.907}$), the vectorial projection of the quadratic hyperpolarizability tensor along the dipole moment direction, has been obtained by working with a fundamental incident wavelength of 1.907 μm (Table 6). In this way the second harmonic ($\lambda/2 = 953$ nm) is quite far from any significant absorption band (Table 3) so that any resonance enhancement is minimized.[36] In parallel, we determined the quadratic hyperpolarizability β_{CT} along the major charge-transfer transitions by a solvatochromic investigation, as an additional way to investigate the charge-transfer origin of the second-order NLO response and consequently the contribution of each significant electronic transition which can be attributed to a charge-transfer process.[19] Of course, $\beta_{1.907}$ and β_{CT} can be compared only when the charge-transfer processes, involved in the second-order NLO response, are close in direction to the dipole moment axis. As can be inferred from Table 6, in all of the complexes **1**−**4** both $\beta_{1.907}$ and β_{CT} have negative signs and comparable absolute values. This suggests that the major charge-transfer transitions are almost parallel to the dipole moment axis, although due to a small but significant orthogonal contribution to the total dipole moment, for instance, in complexes carrying the *cis*-$M(CO)_2Cl$ moiety,[3] the W−M axis (M = Rh, Ir, Ru, Os), where the charge transfer transitions are probably located, cannot perfectly correspond to the dipole moment axis. However, along the W−M axis is located the major component of the dipole moment. Complexes **1**−**4**, if compared to $[W(CO)_4(phen)]$, have slightly lower dipole moments but increased absolute values of both $\beta_{1.907}$ and β_{CT}, which maintain the negative sign as expected if the phenanthroline ligand still behaves as a good σ donor in the ground state and as a significant π acceptor in the MLCT processes (Table 6). The very slight decrease of the dipole moment suggests that the dipolar contributions of the metal−metal bond and of the "*cis*-$M(CO)_2Cl$" (M = Rh, Ir) and "*fac*-$M(CO)_3Cl_2$" (M = Ru, Os) fragments are very small, providing additional evidence for poorly polar W−M bonds. In $[W(CO)_4(phen)]$ the major contribution to β_{CT} is given by the MLCT absorption band at lower energy (499 nm) characterized, as expected for a $W \rightarrow \pi^*_{\mathrm{phen}}$ charge-transfer process,[9] by a

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[36] Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513.

Table 6. Significant Electronic Spectra, Dipole Moments, EFISH $\beta_{1.907}$ Values in $CHCl_3$, and Solvatochromic β_{CT} Values (Incident Wavelength at 1.907 μm)

compd	λ_{max} (nm)	μ (D)	$\beta_{1.907}$ (10^{-30} esu)	β_{CT} (10^{-30} esu)		$\Delta\mu_{eg}$ (D)	f[a]	a (Å)[b]
[W(CO)$_4$(phen)]	499 (MLCT)	8.4[c]	−13[c,d]	−28		−10.6	0.0771	6.23
[(CO)$_3$(phen)W-*cis*-Rh(CO)$_2$Cl] **1**	444[e] 517 (MLCT)	8.0	−31.7	−3.78 −31.96	−35.7	−4.5 −8.3	0.0377 0.0957	6.84
[(CO)$_3$(phen)W-*cis*-Ir(CO)$_2$Cl] **2**	385[e] 503 (MLCT)	9.1	−25.8	−8.96 −27.14	−36	−4.0 −9.6	0.1672 0.0741	7.12
[(CO)$_3$(phen)W-*fac*-Ru(CO)$_3$Cl$_2$] **3**	412[e] 500 (MLCT)	6.9	−76	−24.8 −36.3	−61.1	−20.2 −24.7	0.1174 0.0422	7.03
[(CO)$_3$(phen)W-*fac*-Os(CO)$_3$Cl$_2$] **4**	406[e] 495 (MLCT)	7.5	−75.6	−38.7 −28.8	−67.5	−18.6 −23.3	0.1260 0.0366	7.30

[a] f is the transition oscillator strength, obtained from the experimental integrated absorption coefficient in $CHCl_3$.[18] [b] The cavity radius a was calculated with the molecular weight method.[18] [c] Reference 8. [d] In CH_2Cl_2. [e] Attributed to an additional MLCT ($M \rightarrow \pi^*_{phen}$).

negative $\Delta\mu_{eg}$ value (difference between excited and ground-state dipole moment), while the absorption band at higher energy (388 nm) (Table 3) is not solvatochromic, as expected for the low charge-transfer character of a $\pi \rightarrow \pi^*$ transition of the unsaturated aromatic system.

In complexes **1**–**4**, in addition to the above MLCT absorption band, there is a new absorption band at higher energy, which we tentatively have attributed to an additional MLCT transition. This band is characterized by a significant negative solvatochromism ($\Delta\mu_{eg} < 0$ being the electron-transfer opposite to the ground-state transfer of the dipole moment), which adds to the negative solvatochromism of the MLCT transition at lower energy, thus increasing the absolute value of β_{CT}. While the absolute value of the contribution to β_{CT} of the lower energy MLCT transition is quite constant in all complexes **1**–**4**, the absolute value of the contribution to β_{CT} of the higher energy MLCT transition increases, as expected, in the series **1** < **2** < **3** < **4** (Table 6). Interestingly, in compound **4** the contribution of this latter band becomes more relevant than that of the MLCT transition at lower energy.

The increase of the absolute value of the quadratic hyperpolarizability $\beta_{1.907}$ from -13×10^{-30} esu for [W(CO)$_4$(phen)] to about -26×10^{-30} or -76×10^{-30} esu for the heteronuclear bimetallic complexes **1**–**4** (Table 6) is much greater than that occurring by the introduction of a strong withdrawing substituent such as the nitro group on the phenanthroline ring (from -13×10^{-30} to -18×10^{-30} esu, as reported in ref 9). This significant increase clearly originates, as our solvatochromic investigation has shown, from an electronic effect due to the presence of a relatively weak W–M bond (M = Rh(I), Ir(I), Ru(II), Os(II)).

Conclusions

Several interesting observations concerning the nature of the new stable nonclassical heteronuclear early–late metal–metal bonds, investigated in this work, have emerged. The fundamentally acid–base nature of the heteronuclear W–M (M = Rh(I), Ir(I), Ru(II), Os(II)) bond is supported by the synthetic method, based on the unexpected σ donor behavior of the "W(CO)$_3$(phen)" moiety, by the easy substitution of this latter moiety, acting as a donor ligand, by more soft ligands, and finally by the decreased oxidability of the W(0) atom upon formation of the metal–metal bond. The metal–metal interactions are in the range of single metal–metal bonds of low polarity, as supported by the X-ray structure and by the slight decrease of the dipole moment on going from [W(CO)$_4$(phen)] to the heteronuclear dimeric complexes **1**–**4**. These latter complexes show in their electronic spectra an additional new band at higher energy, generated by the presence of the metal–metal bond, which, as suggested by the blue-shifted solvatochromism and its significant intensity, was tentatively attributed to a charge-transfer process, such as an additional MLCT ($W \rightarrow \pi^*_{phen}$) transition.

The EFISH and solvatochromic investigations on complexes **1**–**4** have shown an increase of the absolute value of the negative second-order NLO response. This increase, which becomes higher on going from M(I) to M(II) as acceptor centers, is not due to an higher contribution of the lower energy MLCT ($W \rightarrow \pi^*_{phen}$) transition, which remains substantially constant, but to a significant contribution of the new higher energy charge-transfer transition, which increases from compound **1** to compound **4**. In conclusion, an heteronuclear metal–metal bond, even if slightly polar and weak, can produce a significant effect on the second-order nonlinear response.

Finally, our results provide further evidence that in simple organometallic chromophores, molecular structures with modest ground-state dipole moments, as first observed by L. T. Cheng et al.,[9] lead to significant nonlinear responses.

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Supporting Information Available: Crystallographic data for compounds 2 and 4, in electronic files as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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