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Preliminary communication

INFLUENCE OF ELECTRONIC FACTORS ON METAL—METAL STRETCHING FREQUENCIES IN LINEAR TRIMETALLIC SYSTEMS

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Summary

IR stretching frequencies are reported for new linear metal—metal bonds in the complexes $[M''—Au—M'']^-$ ($M'' = Mn(CO)_5$, $Co(CO)_4$, η-$C_5H_5Mo(CO)_3$, η-$C_5H_5Fe(CO)_2$) and correlations are established between oxidation state, coordination number of M' in linear M''—M'—M'' systems ($M' = Pd^{II}$, Pt^{II}, Hg^{II}, Au^I) and the corresponding ν(M'—M'') stretching frequencies.

Amongst the limited number of substrates able to give linear M''—M'—M'' trimetallic chains [1], the new series of dihaloaurate(I) anions $[X—Au—X]^-$ (X = Cl, Br, I) [2] was of particular interest as possible precursor of [M''—Au—M''] systems isoelectronic with M''—Hg—M''. We have found that such systems can be produced by treating $[Et_4N]^+$ or $[n\text{-}Bu_4N]^+[AuX_2]^-$ with the carbonylmetallate anions $[M'']^-$ [3].

All reactions were carried out at dry ice/acetone temperature under purified N_2 in THF distilled over Na/benzophenone prior to use. With $M'' = Mn(CO)_5$ and η-$C_5H_5Mo(CO)_3$, the anion was added dropwise to $[Et_4N][AuCl_2]$ in the molar ratio 2/1 and the mixture allowed to react for 15 to 30 minutes. Pentane was then added to precipitate a crude product from which NaCl was eliminated by washing with deoxygenated water. This afforded the complexes: $[Et_4N][(OC)_5Mn—Au—Mn(CO)_5]$(I) ($\nu$(CO) in THF: 2029s, 1949s, 1920ms cm^{-1}) and $[Et_4N][(\eta\text{-}C_5H_5)(CO)_3Mo—Au—Mo(CO)_3(\eta\text{-}C_5H_5)]$(II) ($\nu$(CO) in THF: 1937m, 1912s, 1833s cm^{-1}).

With the other carbonylmetallate anions we observed extensive reduction to metallic gold. For this reason we used $[Et_4N][AuBr_2]$ in the reaction with $Co(CO)_4^-$. The leaving group Br^- being softer than Cl^-, $AuBr_2^-$ is less easily reduced than $AuCl_2^-$. Thus, we were able to obtain the desired complex: $[Et_4N][(OC)_4Co—Au—Co(CO)_4]$ (III) (ν(CO) in KBr: 2023vs, 1947vs, 1929(sh) cm^{-1}). III decomposes slowly in the solid state (change of colour from white to grey within 30 minutes at —79 °C).

With the strong nucleophile $[\eta\text{-}C_5H_5Fe(CO)_2]^-$ we used $[n\text{-}Bu_4N]$-$[AuBr_2]$ as substrate, the larger cation providing a better stabilisation of the final product. We isolated and characterised the complex: $[n\text{-}Bu_4N]$-$[(\eta\text{-}C_5H_5)(OC)_2Fe\text{—}Au\text{—}Fe(CO)_2(\eta\text{-}C_5H_5)]$ (IV) (ν(CO) in THF: 1923s, 1905m, 1871s cm^{-1}). This reaction could even be carried out at room temperature. Satisfactory elemental analyses were obtained for all compounds.

It appears, therefore, that if the cation plays a significant role in the stabilisation of the final metal—metal bonded compound, the choice of the leaving group (i.e. Cl^- or Br^-) is crucial for the stabilisation of the S_N2 reaction intermediate.

The relatively low ν(CO) frequencies indicate a more pronounced anionic character of the M″ group attached to the Au^I center (as in the case of Pd^{II} or Pt^{II} [1]) than in the Hg^{II} compound [5] for which the CO frequencies are very close to the mean values for the neutral dinuclear carbonyls M″—M″.

The far IR spectra (between 100-200 cm^{-1}) for compounds I to IV show a single strong absorption band which is unambiguously assigned to the ν_{as}(Au—M″) stretching mode [1]. These values are given in Table 1, together with the force constant estimated on the basis of a linear triatomic model [6]. For both the frequencies and the force constants, we obtain the following trend when M″ represents the same metal: $k(\text{Pd—M}'') < k(\text{Pt—M}'') < k(\text{Au—M}'') < k(\text{Hg—M}'')$. This series indicates a strengthening of the metal—metal bond in the order $Pd^{II} < Pt^{II} < Au^{I} < Hg^{II}$.

TABLE 1

METAL—METAL FREQUENCIES (SOLID SAMPLES) AND FORCE CONSTANTS

Compound	Bond	ν_{as}(M′—M″) (cm^{-1})	$k-k_{12}$ (M′—M″) [a] (mdyne $Å^{-1}$)
trans-$PdPy_2[Mn(CO)_5]_2$ [b]	Mn—Pd—Mn	149s	0.35
trans-$PtPy_2[Mn(CO)_5]_2$ [b]	Mn—Pt—Mn	155s	0.50
I	Mn—Au—Mn	185s	0.71
$Hg[Mn(CO)_5]_2$ [c]	Mn—Hg—Mn	188	0.74
trans $PdPy_2[Mo(CO)_3\text{-}\eta\text{-}C_5H_5]_2$ [b]	Mo—Pd—Mo	134s	0.36
trans-$PtPy_2[Mo(CO)_3\text{-}\eta\text{-}C_5H_5]_2$ [b]	Mo—Pt—Mo	144w	0.59
II	Mo—Au—Mo	170s	0.83
$Hg[Mo(CO)_3\text{-}\eta\text{-}C_5H_5]_2$ [c]	Mo—Hg—Mo	178	0.91
trans-$PdPy_2[Co(CO)_4]_2$ [b]	Co—Pd—Co	168s	0.46
trans-$PtPy_2[Co(CO)_4]_2$ [b]	Co—Pt—Co	177s	0.68
III	Co—Au—Co	189s	0.77
$Hg[Co(CO)_4]_2$ [d]	Co—Hg—Co	197	0.85
IV	Fe—Au—Fe	193s	0.78
$Hg[Fe(CO)_2\text{-}\eta\text{-}C_5H_5]_2$ [c]	Fe—Hg—Fe	200	0.84

[a] Only the difference $k-k_{12}$ can be obtained from ν_{as} values and we could not assign the bending mode δ(M″—Au—M″). [b] From ref. 1. [c] From ref. 4. [d] From ref. 5.

The comparison between the ν_{as}(Au—M″) and ν_{as}(Hg—M″) frequencies is particularly significant since the change in the masses of the triatomic chain is negligable. This indicates that the ionic character of the Au—transition metal bond is more pronounced than that of the Hg—transition metal bond. As shown previously, this is confirmed by the lower ν(CO) values in the first case.

We conclude that the following relationships exist:

(i) increase in oxidation state of the central atom from $\mathrm{Au^{I}}$ to $\mathrm{Hg^{II}}$ is accompanied by an increase in metal—metal frequencies:

(ii) increase in coordination number (from a two-coordinated $\mathrm{Hg^{II}}$ to a tetracoordinated $\mathrm{Pd^{II}}$ or $\mathrm{Pt^{II}}$ center) is accompanied by a decrease in metal—metal frequencies.

All previously known compounds containing a gold—transition metal bond have been either of the bimetallic type, e.g. $\mathrm{L\rightarrow Au{-}Mn(CO)_5}$ [7,8] or of the osmium—gold cluster type [9]. The $\mathrm{[Et_4N]^+}$ or $\mathrm{[\textit{n}\text{-}Bu_4N]^+}$ $\mathrm{[M''{-}Au{-}M'']^-}$ trimetallic complexes are therefore the first examples of linear, two coordinated gold(I)—transition metal derivatives and appear analogous to the $\mathrm{[Ag\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]^-}$ ions (M = Mo, W) described recently [10] (but for which no metal—metal stretching frequencies were reported).

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