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Cationic Trinuclear 48-Electron Ruthenium Carbonyl Cluster Complexes Containing No Hydride Ligands

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Introduction

In previous papers, we reported that the carbonyl cluster compound $[\mathrm{Ru_3}(\mu\text{-H})(\mu_3\text{-ampy})(\mathrm{CO})_9]$ (**1**; Hampy = 2-amino-6-methylpyridine) reacts with diphenylacetylene to give the alkenyl-bridged derivative $[\mathrm{Ru_3}(\mu_3\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(\mathrm{CO})_8]$ (**2**)[1,2] and that complex **2** can be protonated with $\mathrm{HBF_4{\cdot}OEt_2}$ to give $[\mathrm{Ru_3}(\mu\text{-H})(\mu_3\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(\mathrm{CO})_8][\mathrm{BF_4}]$ (**3**) (Scheme 1).[2a] The presence of the alkenyl and hydride ligands in complex **3** prompted us to study reactions which might induce the reductive elimination of *cis*-stilbene and that would lead to cationic cluster compounds containing no hydride ligands.

Simple protonation of neutral carbonyl cluster complexes frequently leads to hydridic cationic derivatives.[2,3] However, in contrast with the great number of neutral and anionic carbonyl cluster compounds reported to date,[4] very few nonhydridic cationic carbonyl clusters have been described.[5−8] As far as we are aware, and with the exception of the 50-electron compound $[\mathrm{Ru_3}(\mu\text{-PPh_2})_3(\mathrm{CO})_9]^+$,[5] all of the other nonhydridic cationic carbonyl cluster complexes are either 47-electron trinuclear cyclopentadienyl derivatives prepared by chemical or electrochemical oxidation of neutral 48-electron precursors (restricted to a few cobalt complexes[6] and only one of ruthenium[7]) or heteronuclear compounds resulting from the addition of $[\mathrm{M(PR_3)}]^+$ (M = Cu, Ag, Au) to neutral precursors.[8]

We now report the synthesis and some reactivity of $[\mathrm{Ru_3}(\mu_3\text{-ampy})(\mathrm{CO})_{10}][\mathrm{BF_4}]$ (**4**), the first cationic 48-electron trinuclear carbonyl cluster bearing no hydride ligands.

Experimental Details

General Data. Solvents were dried over sodium diphenylketyl (THF, diethyl ether, hydrocarbons) or $\mathrm{CaH_2}$ (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk−vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Compound **1** was prepared as described previously.[9] All other reagents were used as received from Aldrich. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm $\mathrm{CaF_2}$ cells. ^{1}H, ^{13}C, and ^{31}P NMR spectra were run with a Bruker AC-300 instrument, using $\mathrm{SiMe_4}$ (internal, ^{1}H and ^{13}C) or 85% aqueous $\mathrm{H_3PO_4}$ (external, ^{31}P) as standard ($\delta = 0$ ppm). Microanalyses were obtained from the University of Oviedo Analytical Service. GC analyses were carried out at 175 °C on a Perkin-Elmer 8600 gas chromatograph, equipped with a 12-m AQ2 capillary column (i.d. 0.22 mm) and a flame ionization detector. The X-ray diffraction study was carried out using an Enraf-Nonius CAD4 diffractometer. Calculations were made on a MicroVAX-3400 computer at the Scientific Computer Centre of the University of Oviedo.

One-Pot Synthesis of $[\mathrm{Ru_3}(\mu_3\text{-ampy})(\mathrm{CO})_{10}][\mathrm{BF_4}]$ (4). A solution of complex **1** (500 mg, 0.746 mmol) and diphenylacetylene (133 mg, 0.746 mmol) in THF (50 mL) was stirred under nitrogen at reflux temperature for 75 min to give a deep-red solution. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (20 mL). Dropwise addition of $\mathrm{HBF_4{\cdot}OEt_2}$ (ca. 0.5 mL) over 15 min caused a color change from deep-red to brown. Then, carbon monoxide was bubbled for 30 min; a color change from brown to red was accompanied by the precipitation of red crystals. The solvent was removed under reduced pressure and the residue washed with diethyl ether (3 × 10 mL) and dried under vacuum to give complex **4** as a red-orange solid (537 mg, 93%). Anal. Found: C, 24.62; H, 0.92; N, 3.39. Calcd for $\mathrm{C_{16}H_7BF_4N_2O_{10}Ru_3}$: C, 24.73; H, 0.91; N, 3.60. IR ($\mathrm{CH_2Cl_2}$), ν(CO): 2120 (w), 2095 (m), 2078 (vs), 2050 (m), 2027 (m), 1922 cm^{-1} (w, br). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 295 K, 300.13 MHz): 7.63 (t, $J = 7.9$ Hz, 1 H), 7.22 (d, $J = 7.9$ Hz, 1 H), 7.07 (d, $J = 7.9$ Hz, 1 H), 6.49 (s, br, 1 H, NH), 2.82 (s, 3 H) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 200 K, 75.5 MHz): 195.2 (s), 192.6 (s) (carbonyl ligands), 173.8 (s), 160.4 (s), 141.3 (s), 123.3 (s), 114.2 (s), 31.2 (s) (ampy ligand) ppm.

$[\mathrm{Ru_3}(\mu_3\text{-ampy})(\mathrm{CO})_9(\mathrm{PPh_3})][\mathrm{BF_4}]$ (5). Triphenylphosphine (67.5 mg, 0.258 mmol) was added to a solution of complex **4** (200 mg, 0.258 mmol) in 1,2-dichloroethane (20 mL). After the mixture was stirred at room temperature for 1 h, the solvent was removed under reduced pressure and the residue washed with diethyl ether (2 × 5 mL) and dried under vacuum to give complex **5** as a dark-red solid (209 mg, 80%). Anal. Found: C, 38.83; H, 2.32; N, 2.57. Calcd for $\mathrm{C_{33}H_{22}BF_4N_2O_9PRu_3}$: C, 39.18; H, 2.19; N, 2.77. IR ($\mathrm{CH_2Cl_2}$), ν(CO): 2120 (vw), 2098 (m), 2077 (m), 2067 (vs), 2030 (m), 1908 cm^{-1} (w, br). ^{1}H NMR ($\mathrm{CDCl_3}$, 295 K, 300.13 MHz): 7.64−7.27 (m, 15 H), 7.17 (t, $J = 7.8$ Hz, 1 H), 6.86 (d, $J = 7.8$ Hz, 1 H), 6.04 (d, $J = 7.8$ Hz, 1 H), 4.99 (d, br, $J = 3.9$ Hz, 1 H, NH), 2.69 (s, 3 H) ppm. Selected $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR data ($\mathrm{CDCl_3}$, 295 K, 75.5 MHz): 217.5 (d, $J = 5.0$ Hz), 216.2 (d, $J = 5.0$ Hz), 199.4 (d, $J = 4.5$ Hz), 196.4 (d, $J = 4.5$ Hz), 195.6 (s), 193.8 (s), 190.5 (s), 188.9 (s), 181.3 (s) (nine carbonyl ligands), 173.7 (s), 158.8 (s), 140.2 (s), 121.6 (s), 114.1 (s), 29.9 (s) (ampy ligand) ppm. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 295 K, 121.5 MHz): 33.89 (s) ppm.

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Scheme 1

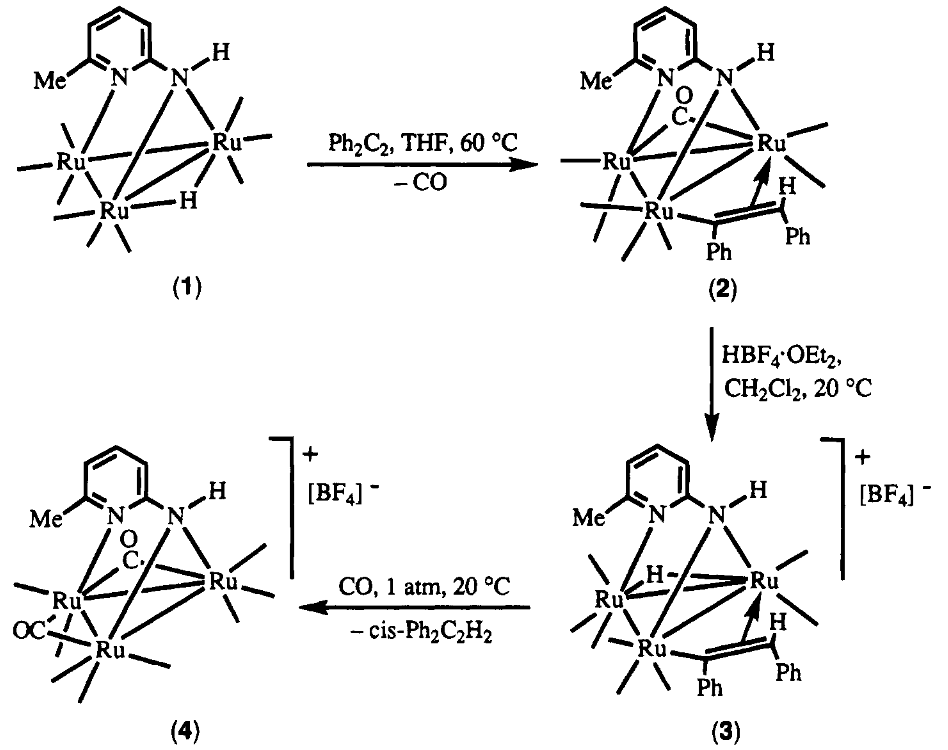

Table 1. Selected Crystallographic Data for $5 \cdot C_5H_{12}$

formula	$C_{33}H_{22}BF_4N_2O_9PRu_3 \cdot C_5H_{12}$
fw	1083.66
cryst syst	triclinic
space group	$P\bar{1}$
a, b, c, Å	10.234(5), 11.359(3), 18.331(6)
α, β, γ, deg	81.66(3), 82.42(5), 74.93(5)
V, Å^3	2026.1(13)
Z	2
T, K	200(2)
λ, Å	0.710 73
D_{calcd}, g/cm^3	1.776
μ, cm^{-1}	12.17
$R(F)_{I>2\sigma(I)}$ [a]	0.0287
$R_w(F^2)_{all\ data}$ [b]	0.0750

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

[Ru$_3$(μ_3-ampy)(CO)$_8$(PPh$_3$)$_2$][BF$_4$] (6). A solution of triphenylphosphine (33.8 mg, 0.129 mmol) and complex **4** (50 mg, 0.064 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 15 min. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2 × 5 mL) and dried under vacuum to give complex **6** as a dark-red solid (60 mg, 75%). Anal. Found: C, 48.32; H, 3.10; N, 2.20. Calcd for $C_{50}H_{37}BF_4N_2O_8P_2Ru_3$: C, 48.21; H, 2.99; N, 2.25. IR ($C_2H_4Cl_2$), ν(CO): 2078 (s), 2025 (vs), 1998 (sh), 1974 (w), 1858 cm^{-1} (w, br). ^{1}H NMR (CDCl$_3$, 295 K, 300.13 MHz): 7.69 (t, J = 7.6 Hz, 1 H), 7.58–7.12 (m, 30 H), 6.92 (d, J = 7.6 Hz, 1 H), 5.02 (d, J = 7.6 Hz, 1 H), 3.78 (s, br, 1 H, NH), 2.78 (s, 3 H) ppm. Selected ^{13}C{^{1}H} NMR data (CDCl$_3$, 295 K, 75.5 MHz): 236.6 (t, J = 7.0 Hz, 2 C), 202.8 (s, 1 C), 199.5 (t, J = 3.8 Hz, 2 C), 196.8 (s, 1 C), 193.8 (s, 2 C) (eight carbonyl ligands), 172.8 (s), 159.7 (s), 140.9 (s), 121.7 (s), 112.4 (s), 30.1 (s) (ampy ligand) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 295 K, 121.5 MHz): 33.90 (s) ppm.

Crystal Structure of $5 \cdot C_5H_{12}$. A dark red crystal of $5 \cdot C_5H_{12}$, obtained by layering pentane on a solution of the complex in dichloromethane, was used for the X-ray diffraction study. A selection of crystal and refinement data is given in Table 1.

The cell dimensions were determined by least-squares refinement of 25 reflections with $15 < \theta < 20°$; space group $P\bar{1}$ from structure determination; 7378 reflections measured. The intensities were collected using the $\omega - 2\theta$ scan technique with a variable scan rate and a maximun scan time of 60 s per reflection. Three standard reflections were monitored every 60 min, revealing no intensity fluctuations. Final drift correction factors were between 0.95 and 1.04. Profile analysis was performed on all reflections.[10] Empirical absorption correction based on ψ scans applied[11] was μ(Mo Kα) = 12.17 cm^{-1} (minimum, maximum correction factors 0.995, 1.000). Some doubly measured reflections averaged, $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I = 0.024$, to give 7122 unique reflections from which 5504 were considered observed with $I > 2\sigma(I)$. Lorentz and polarization corrections were applied and data reduced to $|F_o|$ values.

The structure was solved by Patterson interpretation using DIRDIF92.[12] Isotropic least-squares refinement, using a local version[13] of SHELX,[14] was followed by a semiempirical absorption correction[15] (maximum and minimum correction factors 0.53 and 0.49, respectively). Full-matrix anisotropic least-squares refinement over F^2, using the program SHELXL93,[16] followed by a difference Fourier synthesis allowed the location of all the hydrogen atoms. After refinement of the positional and anisotropic thermal parameters of the non-hydrogen atoms, the hydrogen atoms were refined isotropically with a common thermal parameter and with free coordinates, except those of the methyl group, which were refined by constraining distances to their parent atom and left riding with free rotation. A disordered pentane solvent molecule was refined with a restaint model, refining the occupation factors of two components as p and 1-p, restraining chemically equivalent 1–2, 1–3, and 1–4 distances to be equal for the two components, and restraining the displacement parameters along the bond directions for all atoms to be equal. Function minimized: $\Sigma w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2$-

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Scheme 2

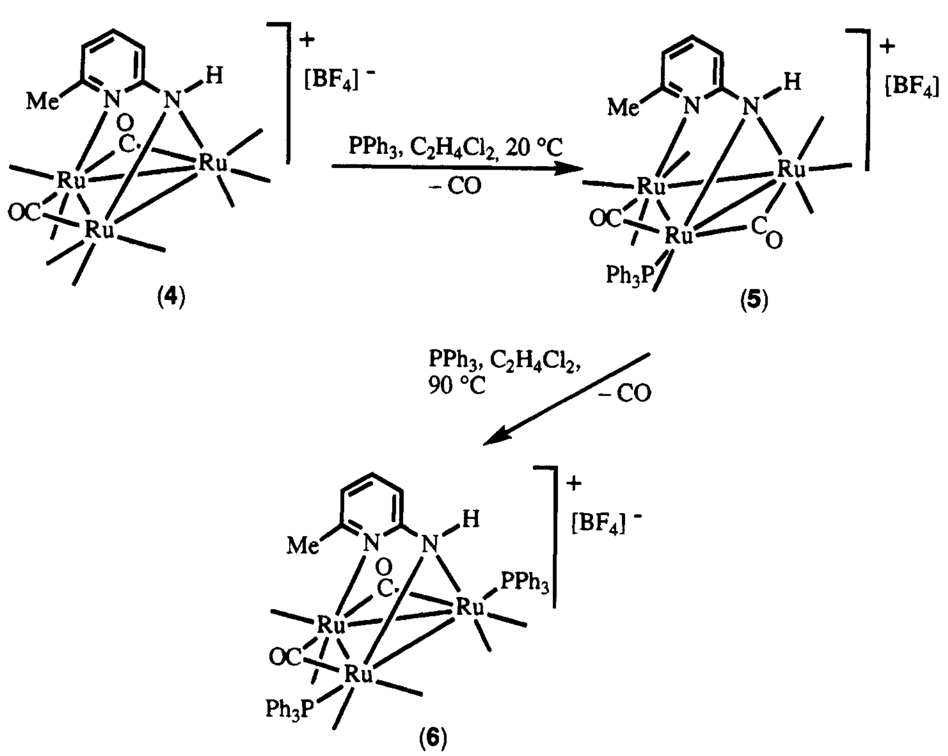

Table 2. Positional Parameters ($\times 10^4$) for Selected Atoms of $\mathbf{5}\cdot C_5H_{12}$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ru(1)	441(1)	1786(1)	1316(1)
Ru(2)	1368(1)	1247(1)	2671(1)
Ru(3)	1831(1)	3317(1)	1760(1)
P(1)	2380(1)	−644(1)	3374(1)
N(1)	2290(3)	626(3)	1642(2)
N(2)	3594(3)	2062(3)	1249(2)
C(1)	−1236(4)	3016(4)	1267(2)
C(2)	−329(4)	548(3)	1008(2)
C(3)	1077(4)	2276(3)	320(2)
C(4)	−321(4)	851(3)	2484(2)
C(5)	283(5)	2029(4)	3455(2)
C(6)	2823(5)	1970(3)	2865(2)
C(7)	1471(4)	4394(3)	860(2)
C(8)	2795(5)	4316(4)	2159(2)
C(9)	179(5)	4171(4)	2221(2)
O(1)	−2211(3)	3753(3)	1252(2)
O(2)	−855(3)	−105(3)	829(2)
O(3)	1499(3)	2503(3)	−265(2)
O(4)	−1327(3)	551(3)	2649(2)
O(5)	-409(4)	2554(3)	3901(2)
O(6)	3639(4)	2132(3)	3175(2)
O(7)	1237(3)	5028(3)	344(2)
O(8)	3243(4)	4918(3)	2440(2)
O(9)	−823(3)	4700(3)	2492(2)

$(F_o^2) + (0.0435P)^2]$, with $\sigma(F_o)$ from counting statistics and $P = (F_o^2 + 2F_c^2)/3$. Maximum shift over error ratio in the last full-matrix least-squares cycle was less than 0.08. Atomic scattering factors were taken from ref 17. Geometrical calculations were made with PARST,[18] and the structure plot was drawn with the EUCLID package.[19] Final atomic coordinates are given in Table 2.

Results and Discussion

The cationic hydrido−alkenyl complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_8][BF_4]$ (**3**; Scheme 1) released *cis*-stilbene (GC identification) upon reaction with carbon monoxide under mild conditions (CO bubbled, room temperature) to give complex **4**, quantitatively. This cationic compound can also be prepared in a one-pot synthesis (93% isolated yield) starting from $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**1**; Scheme 1). The ionic nature of this compound was clearly evidenced by the presence of typical $[BF_4]^-$ bands in its IR spectrum and by the high wavenumbers of its ν(CO) absorptions (terminal CO's, 2120−2027 cm^{-1}; bridging CO's, 1922 cm^{-1}).

A variable-temperature ^{13}C NMR study indicated CO scrambling even at 200 K (low solubility prevented measurements at lower temperatures). Interestingly, anionic trimetal clusters containing μ_3-capping ligands are much more dynamic than their neutral hydride parent compounds;[20] this seems to be also the case for their cationic counterparts.

Unfortunately, no single crystals of compound **4** suitable for an X-ray diffraction study could be obtained; therefore, in order to shed light on the structural characteristics of this compound, its reactivity with phosphine ligands was studied. Complex **4** reacted with 1 and 2 equiv of triphenylphosphine to give mono- (**5**) and disubstituted (**6**) derivatives, respectively (Scheme 2). Both compounds showed bridging CO absorptions in their IR spectra and proved to be stereochemically rigid at room temperature, since their ^{13}C NMR spectra showed nine (**5**) and five (**6**) CO resonances (indicating asymmetrical (C_1) nonacarbonyl and symmetrical (C_s) octacarbonyl trinuclear derivatives, respectively). In hydridic cluster compounds, phosphine substitution generally results in a slowing down of the carbonyl fluxionality, but this in not always the case for nonhydridic trimetal clusters.[21]

The pentane solvate $\mathbf{5}\cdot C_5H_{12}$ was structurally characterized by X-ray diffraction methods (Figure 1). The cation consists of a triangular array of ruthenium atoms, Ru(1)−Ru(2) 2.705-

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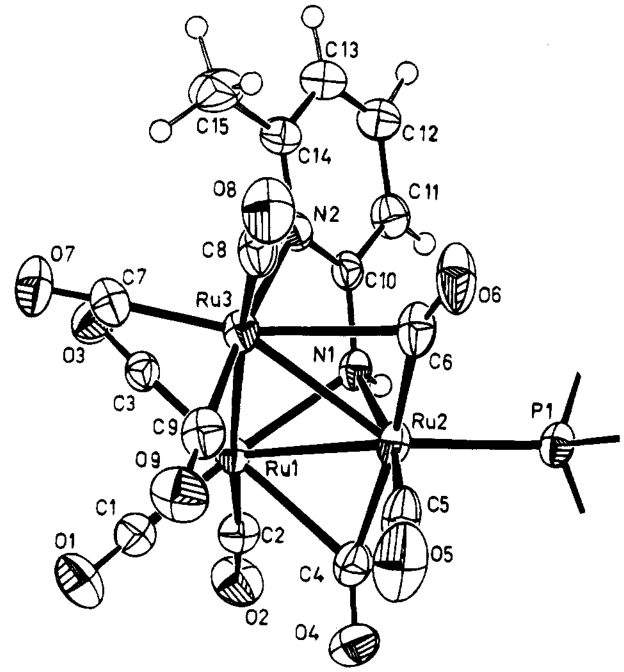

Figure 1. Structure of the cation $[Ru_3(\mu_3\text{-ampy})(CO)_9(PPh_3)]^+$ in $\mathbf{5}{\cdot}C_5H_{12}$. Phenyl groups have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

(1) Å, Ru(1)–Ru(3) 2.778(1) Å, Ru(2)–Ru(3) 2.789(1) Å, triply bridged by the ampy ligand, with the PPh_3 group attached to the Ru(2) atom, Ru(2)–P(1) 2.396(2) Å, in an equatorial site cis to two semibridging CO ligands, Ru(2)–C(4) 1.978(4) Å, Ru(1)–C(4) 2.377(4) Å, Ru(2)–C(6) 1.970(4) Å, Ru(3)–C(6) 2.512(4) Å. The ligand shell of the cluster is completed by three axial and four equatorial CO ligands. This structural study, in addition to locating the positions of all the ligands in complex **5**, suggests that the high-wavenumber bands observed for the bridging CO ligands in the IR spectra of compounds **4**–**6** may be due not only to the cationic nature of the complexes but also to a semibridging character of these ligands. It is interesting to note that the structural parameters of complex **5** do not differ significantly from those of related phosphine-substituted triruthenium hydride carbonyl clusters containing the ampy ligand.[3b,c]

The structure of compound **5** and the structural symmetry indicated by the ^{13}C and ^{31}P NMR spectra of compound **6** strongly support the structure depicted for complex **6** in Scheme 2. Moreover, if the disubstituted complex **6** is symmetrical, the unsubstituted complex **4** should probably have the same symmetrical structure (Schemes 1 and 2).

In conclusion, this paper reports a high-yield synthesis of a so far rare example of a 48-electron cationic cluster compound containing no hydride ligands. We anticipate that the synthetic strategy described above (reaction of a neutral hydrido cluster with an alkyne, followed by protonation under CO) may be a simple and efficient entry into the chemistry of nonhydridic cationic carbonyl cluster compounds. This class of complexes are expected to have an enhanced reactivity toward nucleophilic reagents (easy ligand substitution,[5] nucleophilic addition to coordinated CO ligands,[3c] synthesis of large clusters by reaction with anionic clusters,[22] etc).

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Supplementary Material Available: Tables of crystal data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for $\mathbf{5}{\cdot}C_5H_{12}$ (13 pages). Ordering information is given on any current masthead page.

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