Quintuple Bond

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Haloacylation of the Quintuple-Bonded Group VI Metal Amidinate Dimers and Disproportionation of Acyl Groups to Form Carbynes**

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Dedicated to Professor Shie-Ming Peng on the occasion of his 65th birthday

The addition of acyl chloride to alkynes is not only of fundamental interest, but also important in chemical and pharmaceutical industries, because both carbonyl and chloro functionalities are simultaneously introduced to yield β-chloro α,β-unsaturated ketones.[1] Many N- and O-containing heterocycles of industrial importance have been subsequently prepared from these ketones.[1,2] β-Chlorovinyl ketones are readily synthesized from alkynes and under acyl chlorides under the traditional Friedel–Crafts conditions.[1,3]

Like the C−C π bond, the metal–metal δ bond is a two-electron two-center bonds formed by the highest occupied molecular orbital,[4] thus the reactivity of quadruple-bonded dinuclear complexes has been highly anticipated. Although a large number of quadruple-bonded dinuclear species have been characterized in the past five decades,[5] their reactivity is far less explored. After a long hiatus, interest in metal–metal multiple bonding was reinvigorated by Power and co-workers who reported the first Cr−Cr quintuple bonded compounds.[6] This field was propelled by the identification of few nitrogen-donor-stabilized quintuple bonded Group VI compounds.[7] These low-coordinate quintuple-bonded species not only have interesting metal–metal bonding, but also show remarkable reaction chemistry.[8–16] Recent studies have indicated that there are strong analogies between the δ component of the metal–metal quintuple bonds and the π component of the carbon–carbon multiple bonds. For example, the quintuple bonded molybdenum amidinate dimers $[Mo_2\{\mu\text{-}\kappa^2\text{-}RC(N\text{-}2,6\text{-}i Pr_2C_6H_3)_2\}_2]$ (R = H (**1**), Ph)[17] react with two equivalents of terminal alkynes to give the first aromatics containing two multiple-bonded dimetal units by a [2+2+2] cycloaddition process,[14] while its chromium analogue $[Cr_2\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i Pr_2C_6H_3)_2\}_2]$ (**2**)[18] reacts with alkynes to afford [2+2] adducts. Kempe and co-workers have described that the carboalumination, one characteristic reaction of alkenes and alkynes,[19] also occurs to the Cr−Cr quintuple bond.[13] These reactivity analogies between p_π and d_δ systems inspired us to explore functionalization of the metal–metal quintuple bonds.

We herein report the first example of Friedel–Crafts-type haloacylation of the metal–metal quintuple bond to yield β-halo α,β-quadruple-bonded dimolybdenum acyl complexes. These β-halo dimolybdenum acyls are reactive and subsequently react with aroyl halides to yield three-membered dimolybdenum arylidyne heterocyclic compounds via an unprecedented acyl disproportionation.

As illustrated in Scheme 1, exposure of acid halides RCOX (R = C_6H_5, 2-MeC_6H_4, Me; X = Cl, Br) to **1** in a 1:1 stoichiometric ratio at room temperature in diethyl ether for 10 min gives only one product (**3**–**6**) for each acid halide, as shown by ^{1}H NMR spectroscopy. Four septet signals corresponding to the methine hydrogen atoms of eight isopropyl groups suggest two Mo atoms with different coordination environments. Additionally, strongly deshielded acyl carbonyl carbon resonance signals at $\delta = 295.5$ (**3**), 285.0 (**4**), 291.9 (**5**), and 241.3 ppm (**6**) in the ^{13}C NMR are assigned to the η^2-acyl moieties. These spectroscopic data suggest that the Mo^I–Mo^I quintuple bond of **1** inserts into the C−X bonds of acyl halides and exclusively gives the halo- and acyl-substituted Mo^{II}–Mo^{II} quadruply bonded complexes $[Mo_2(X)(\mu\text{-}\kappa^2\text{-}OCR)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i Pr_2C_6H_3)_2\}_2]$ (X = Cl, R = C_6H_5 (**3**), 2-MeC_6H_4 (**5**); X = Br, Ar = C_6H_5 (**4**); X = Cl, R = CH_3 (**6**)) in good yields (see the Supporting Information). Complexes **3**–**6** are robust and do not undergo decarbonylation upon heating.

The molecular structures of **4** and **5** were determined by single crystal X-ray crystallography,[20] and **4** is depicted in Figure 1, while **5** having two independent molecules in a unit cell is shown in Figure S1. Complexes **4** and **5** have similar structures. Besides two bridging amidinates, Mo1 is terminally ligated by a halide, and Mo2 is bound by an aroyl ligand from the opposite hemisphere with its oxygen atom coordinating to Mo1. As a result, both **4** and **5** show a *trans-cisoid* configuration, whereas *trans* β-chlorovinyl ketones display a *trans-transoid* conformation. The carbonyl carbon atom of the acyl group is attached to only one Mo atom and forms a Mo−C single bond, and the oxygen atom closes the bridge binding the other Mo atom. The slightly long C=O double bonds (1.282(4) Å (**4**) and 1.278(6) and 1.285(6) Å (**5**)) and short Mo−C single bonds suggest an enolate character. All three Mo−Mo bond lengths (Mo1−Mo2 2.0717(5) Å (**4**), Mo1−Mo2 2.1115(6) Å, and Mo3−Mo4 2.1099(6) Å (**5**)) in

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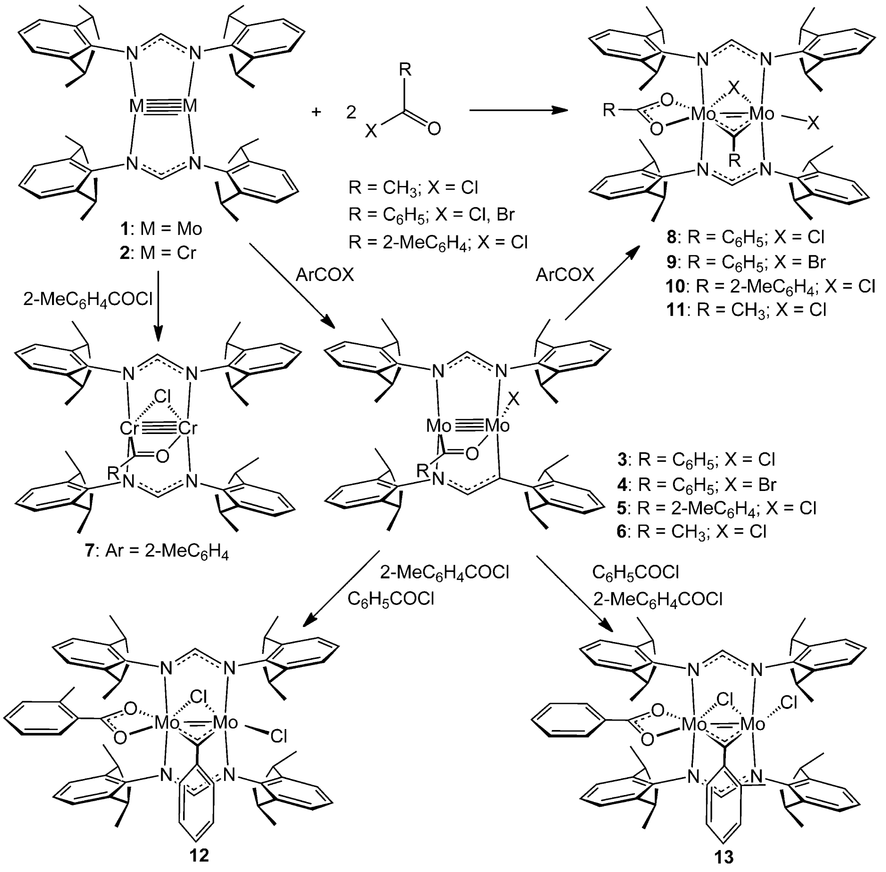

Scheme 1. Synthesis of compounds **3**–**13**.

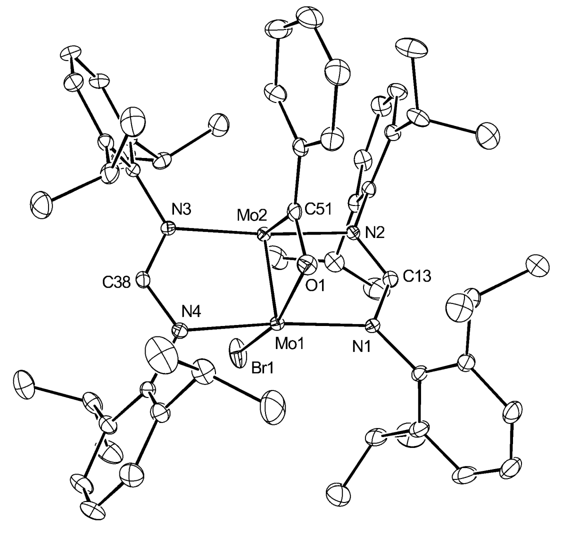

Figure 1. The solid-state molecular structure of **4**, thermal ellipsoids set at 35% probability. Selected bond lengths [Å] and angles [°]: Mo1-Mo2 2.0717(5), C51-Mo2 2.135(4), C51-O1 1.282(4), O1-Mo1 2.293(2), Mo1-Br 2.6231(6), N1-Mo1 2.128(3), N4-Mo1 2.129(3), N2-Mo2 2.125(3), N3-Mo2 2.130(3); O1-Mo1-Br1 163.60(6).

both compounds are within the range expected for a typical Mo–Mo quadruple bond.[5,21]

Metal acyls are important intermediates in many metal-mediated carbonylation reactions in organometallic chemistry and catalysis.[22] They are usually prepared either through addition of acyl halides to low-valent metal complexes[23] or by insertion of carbon monoxide into metal alkyl bonds.[22] The reactions leading to **3**–**5** represent a remarkable example that the metal–metal quintuple bonded compound can undergo the alkyne-like addition reactions. Noteworthy is that although β-chloro α,β-unsaturated ketones can be easily prepared from the addition of acid chlorides to alkynes, the products usually suffer from mixtures of *E* and *Z* isomers.[1,2] Presumably, the coordination of the C=O functionality to the Mo–Mo quintuple bond, which blocks one hemisphere, facilitates high stereoselectivity in **3**–**5**. No solvent effect is observed for these reactions, since they proceed fast (under 10 min) in nonpolar *n*-hexane as well, which suggests the addition of C–X to the Mo–Mo quintuple bond is likely through a concerted mechanism. On the other hand, a chloride-bridged chromium analogue $[Cr_2(\mu\text{-}Cl)(\mu\text{-}\kappa^2\text{-}OC\text{-}2\text{-}MeC_6H_4)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}iPr_2C_6H_3)_2\}_2]$ (**7**) is actually obtained in a quantitative yield form the reaction of **2** and *o*-toluoyl chloride in *n*-hexane and its crystal structure is depicted in Figure S2. It is interesting to note that **7** quickly decomposes upon exposure to THF.

We wondered if the synthesized β-halo α,β-quadruple bonded dimetal acyls **3**–**7** would undergo cyclization to furnish heterocycles. In light of the slight enolate character of aroyl groups in **4** and **5**, **3**–**7** were treated with one equivalent of acyl halides as illustrated in Scheme 1. Addition of one equivalent of C_6H_5COX, where X = Cl, Br, to an ethereal solution of **3** and **4**, respectively, elicits a quick color change to royal purple at room temperature. As indicated by ^{1}H NMR spectroscopy, both of these two reactions proceed cleanly and unexpectedly yield solely the benzylidyne products $[Mo_2(X)(\mu\text{-}X)(\mu\text{-}CPh)(\kappa^2\text{-}O_2CPh)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}iPr_2C_6H_3)_2\}_2]$ (X = Cl (**8**), Br (**9**)) in good yields after 0.5 h stirring.[24,25] The steric effect is observed when **5** is treated with 1 equivalent of *o*-toluoyl chloride in diethyl ether, the bridging benzylidyne species $[Mo_2(Cl)(\mu\text{-}Cl)(\mu\text{-}C\text{-}2\text{-}MeC_6H_4)(\kappa^2\text{-}O_2C\text{-}2\text{-}MeC_6H_4)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}iPr_2C_6H_3)_2\}_2]$ (**10**) is also formed, but to expedite this reaction, it is carried out at 60 °C for 4 h to reach completion. Alternatively, the benzylidynes **8**–**10** can be directly prepared in good yields from the reactions of **1** with two equivalent of aroyl halides. The ^{1}H NMR spectra of compounds **8**–**10** in C_6D_6 show only one resonance peak for the methine hydrogen atoms of the amidinato ligand backbones. In addition, four septet signals corresponding to the four methine hydrogen atoms of eight *i*Pr substituents suggest that the benzylidynes **8**–**10** feature an unsymmetrical molecular conformation. The ^{13}C NMR spectroscopy show strongly deshielded resonance signals at $\delta =$ 409.6 (**8**), 406.9 (**9**), and 398.8 ppm (**10**) corresponding to the bridgehead carbon atoms of the carbyne ligands. Such aroyl disproportionation also occurs to an alkyl acyl group. The ethylidyne derivative $[Mo_2(Cl)(\mu\text{-}Cl)(\mu\text{-}CCH_3)(\kappa^2\text{-}O_2CCH_3)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}iPr_2C_6H_3)_2\}_2]$ (**11**) is obtained by treating **1** with two equivalents of acetyl chloride. To our surprise, **7** is unreactive towards common acyl halides. This inactivity is presumably due to the lower nucleophilicity (enolate) of the oxygen atom in the chromium acyl Cr–C(O)Ar, suggested by the normal Cr–C single bond (2.060(5) Å) and C=O double bond (1.254(6) Å).

The formulations of **8**, **9** and **11** are supported by single-crystal X-ray analysis. The molecular structure of **9** is presented in Figure 2, while the molecular structures of **8** and **11** are depicted in Figure S3 and S4, respectively. Two Mo atoms of **8**, **9**, and **11** are spanned by two amidinates, a halogen atom, and a carbyne group. Additionally, one of two Mo atoms is ligated by a halo ligand and the other is chelated by an unexpected carboxylato group, thereby giving unsymmetrical dimolybdenum complexes, consistent with the NMR spectra. All three compounds show short Mo–C(carbyne) bond lengths of 2.004(5) and 1.942(4) Å in **8**, 1.989(4) and 1.938(4) Å in **9**, and 1.930(8) and 1.907(8) Å in **11**, consistent with the expected formal bond order of 1.5 in a symmetrically bridging carbyne ligand.[26] **8**, **9** and **11** also have very short Mo = Mo double bonds, 2.4343(6), 2.4624(4), and 2.4486(9) Å, respectively, much shorter than the reported Mo=Mo double bond lengths in the range of 2.58 and 2.62 Å.[27]

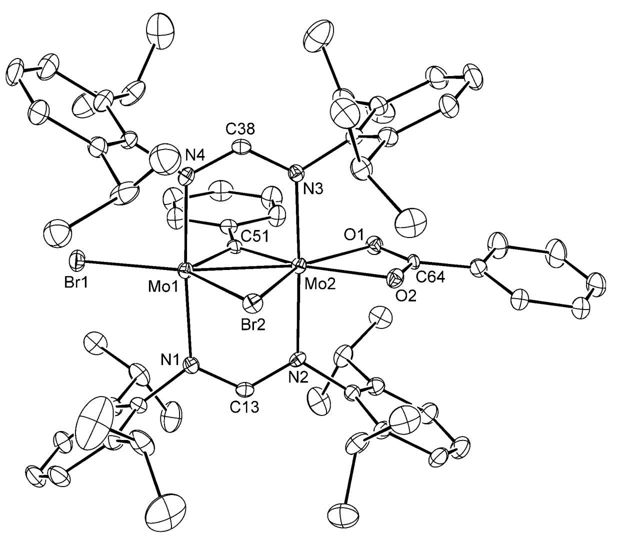

Figure 2. The solid-state molecular structure of complex **9**, thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1-Mo2 2.4624(4), C51-Mo1 1.938(4), C51-Mo2 1.989(4), N1-Mo1 2.146(3), N4-Mo1 2.142(3), N2-Mo2 2.136(3), N3-Mo2 2.115(3); Mo1-C51-Mo2 77.67(15), Br1-Mo1-Mo2 157.29(2).

The identification of **8**–**11** represents the first examples whereby the carbyne ligands are generated from acyl disproportionation concomitant with the decrease of the Mo–Mo bond order from 4 to 2 under mild conditions. The quintuple bonded dimolybdenum unit accordingly serves as a 6-electron reductant. Two interesting questions immediately arise, and the first is: Do the carbyne ligands come from the first or second equivalent of acyl halides? To answer this question, we performed two reactions. An ethereal solution of **1** was first treated with 1 equivalent of benzoyl chloride, and then 1 equivalent of *o*-toluoyl chloride after 10 min stirring. The benzylidyne complex $[Mo_2(Cl)(\mu\text{-}Cl)(\mu\text{-}CC_6H_5)(\kappa^2\text{-}O_2C\text{-}2\text{-}MeC_6H_4)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}iPr_2C_6H_3)_2\}_2]$ (**12**) was isolated. On the other hand, if the addition sequence is reversed, we successfully isolate the isomer of **12**, namely, $[Mo_2(Cl)(\mu\text{-}Cl)(\mu\text{-}C\text{-}2\text{-}MeC_6H_4)(\kappa^2\text{-}O_2CC_6H_5)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}iPr_2C_6H_3)_2\}_2]$ (**13**). Both X-ray crystal structures of **12** and **13** are shown in Figure 3. Complex **12** features a bridging benzylidyne and a chelating 2-methylbenzoate, whereas **13**

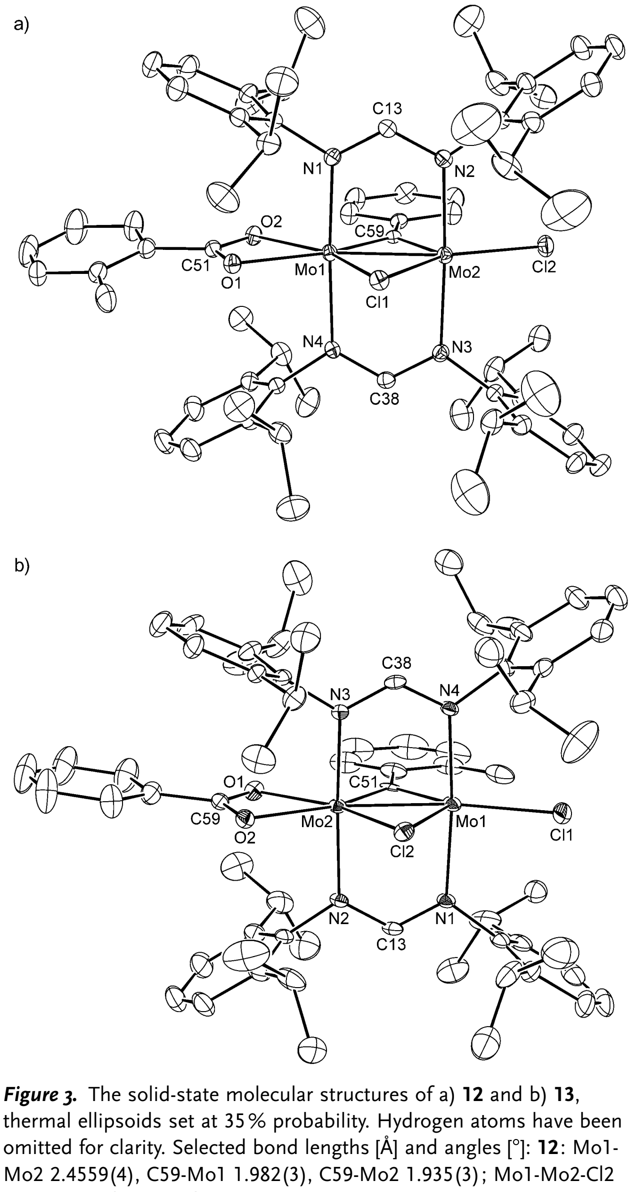

Figure 3. The solid-state molecular structures of a) **12** and b) **13**, thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: **12**: Mo1-Mo2 2.4559(4), C59-Mo1 1.982(3), C59-Mo2 1.935(3); Mo1-Mo2-Cl2 155.07(3), Cl1-Mo2-Cl2 145.59(3); **13**: Mo1-Mo2 2.4823(6), C51-Mo1 1.925(5), C51-Mo2 1.983(4); Mo2-Mo1-Cl1 157.94(4), Cl1-Mo1-Cl2 98.75(5).

bears a 2-methylbenzylidyne and a benzoate group. It is therefore clear that the carbyne ligands in **8–13** are derived from the first equivalent of acyl halides and the carboxylates result from the second molecule of acyl halides by an oxo transfer process. Note that **8–9** and **11–13** are almost isostructural, except that the terminal halogen atoms in **8–9** and **11–12** are oriented *cis* to benzylidyne groups, but the terminal chloro in **13** is *trans* to the more sterically hindered 2-methylbenzylidyne group. Owing to the stronger *trans* influence of the benzylidyne group than the chloride ligand, the Mo2−Cl2 bond length in **12** is 2.3594(9) Å, significantly shorter than the corresponding Mo2−Cl bond length (2.432(4) Å) in **13**. However, the equivalent Mo = Mo double bond lengths of **12** (2.4559(4) Å) and **13** (2.4823(6) Å) are independent of their terminal chloro ligands.

The second question concerns the two distinct halogen atoms (one bridging and one terminal) in **8–13**: Which one is from the first equivalent of acyl halides? It seems natural to interrogate this distinction by first treating **1** in diethyl ether with 1 equivalent of benzoyl chloride and then 1 equivalent of benzoyl bromide after 10 min stirring or the other way around. Unexpectedly, these two reactions are the same according to their product analysis. Both these two reactions furnish four products in a ratio of 1:1:1:1, as assayed by ^{1}H and ^{13}C NMR spectroscopy in a C_6D_6 solution. Complexes **8** and **9** are unexpectedly two of them, and the other two compounds are presumably the two isomers $[Mo_2(X)(\mu\text{-}X')(\mu\text{-}CC_6H_5)(\kappa^2\text{-}O_2CC_6H_5)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{Pr}_2C_6H_3)_2\}_2]$ (X = Cl, X′ = Br (**14**) and X = Br, X′ = Cl (**15**)), where the Cl and Br groups show different coordination modes. These observations suggest that the halo ligands in the benzylidynes $[Mo_2(X)(\mu\text{-}X')(\mu\text{-}CAr)(\kappa^2\text{-}O_2CAr)\{\mu\text{-}\kappa^2\text{-}HC(N\text{-}2,6\text{-}i\text{Pr}_2C_6H_3)_2\}_2]$ undergo not only a rapid intramolecular exchange, but also an intermolecular redistribution. To further substantiate this conclusion, we performed one more experiment by mixing an equal molar amount of **8** and **9** in C_6D_6. This reaction is monitored by ^{1}H NMR spectroscopy at room temperature, and after 13 h an identical ^{1}H NMR spectrum is obtained to that of the reaction of **1** and 1 equivalent of PhC(O)Cl and then 1 equivalent of PhC(O)Br (see Figure S5 in the Supporting Information). Furthermore, the X-ray crystallographic study is also in accordance with the ^{1}H NMR spectra. Recrystallization of the products from the reaction of **1** with benzoyl chloride and then benzoyl bromide from a solution of diethyl ether/*n*-pentane at room temperature furnishes orange crystals suitable for X-ray analysis, and the molecular structure is depicted in Figure S6. This solid-state molecular structure can be viewed as either a mixture of **8** and **9** or **14** and **15** in a ratio of 1:1, because both Br and Cl atoms are disordered in both terminal and bridging positions with the occupancy ratio being 1:1.

In summary, akin to the preparation of β-chloro α,β-unsaturated ketones from alkynes and acyl chlorides by the Friedel–Crafts-type insertion reaction, we have demonstrated such reactions also occur to the amidinate-supported Mo−Mo quintuple bonded dimer **1** under catalyst-free conditions to give exclusively the *trans-cisoid* β-halo α,β-quadruple bonded dimolybdenum acyls **3–6**. Mechanistic elucidation for the formation of **3–6** is reinforced by the characterization of **7**, in which the quadruple bonded dichromium unit is bridged by a chloro ligand. Subsequent reactions of **3–6** with one equivalent of acyl halides resulted in an unprecedented acyl disproportionation and the decrease of the Mo−Mo bond order to give the carbynes **8–13**, which also feature a carboxylate group. The carbyne ligands are produced from the first molecule of acyl halide and the carboxylate groups result from the second acyl substituents by an oxo transfer. We have also demonstrated that because of the strong *trans* effect carbyne groups, the halo ligands in **8–15** are so labile that they undergo rapid intramolecular and intermolecular exchanges. By and large, these results further illustrate that the δ components of the group VI metal quintuple bonds show a close resemblance to the π components of the C−C multiple bonds.

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[20] Crystallographic data for **4**: $C_{57}H_{75}Br\,Mo_2N_4O$: $M_r = 1104.00$, $T = 200(2)$ K, monoclinic, space group $P2_1/c$, $a = 14.855(3)$, $b = 18.257(3)$, $c = 21.137(3)$ Å, $\beta = 109.111(3)°$, $V = 5416.6(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.354$ Mg m^{-3}, $\mu = 1.242$ mm^{-1}, reflections collected: 34677, independent reflections: 9509 ($R_{int} = 0.0460$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0375$, $wR_2 = 0.0879$, R indices (all data): $R_1 = 0.0613$, $wR_2 = 0.1021$; **5**: $C_{58}H_{77}ClMo_2N_4O$: $M_r = 1073.57$, $T = 200(2)$ K, triclinic, space group $P2_1/c$, $a = 21.489(3)$, $b = 21.886(3)$, $c = 23.615(3)$ Å, $V = 10928(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.305$ Mg m^{-3}, $\mu = 0.549$ mm^{-1}, reflections collected: 58894, independent reflections: 19334 ($R_{int} = 0.0725$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0470$, $wR_2 = 0.0981$, R indices (all data): $R_1 = 0.0914$, $wR_2 = 0.1285$; **7**: $C_{58}H_{77}ClCr_2N_4O$ $M_r = 985.69$, $T = 200(2)$ K, monoclinic, space group $P2_1/c$, $a = 14.6041(6)$, $b = 18.1483(7)$, $c = 21.8030(9)$ Å, $\beta = 108.847(2)°$, $V = 5468.8(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.197$ Mg m^{-3}, $\mu = 0.487$ mm^{-1}, reflections collected: 28003, independent reflections: 9598 ($R_{int} = 0.0623$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0671$, $wR_2 = 0.1937$, R indices (all data): $R_1 = 0.1268$, $wR_2 = 0.2469$; **8**·2.7 C_5H_{12}: $C_{77.50}H_{112.40}Cl_2Mo_2N_4O_2$, $M_r = 1394.89$, $T = 200(2)$ K, triclinic, space group $P\bar{1}$, $a = 13.103(2)$, $b = 14.080(2)$, $c = 19.976(3)$ Å, $\alpha = 84.099(3)$, $\beta = 80.683(3)$, $\gamma = 81.330(3)°$, $V = 3583.5(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.293$ Mg m^{-3}, $\mu = 0.472$ mm^{-1}, reflections collected: 20421, independent reflections: 12418 ($R_{int} = 0.0295$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0583$, $wR_2 = 0.1697$, R indices (all data): $R_1 = 0.0822$, $wR_2 = 0.1826$; **9**·4.1 OEt_2: $C_{80.40}H_{121}Br_2Mo_2N_4O_{6.10}$, $M_r = 1592.91$, $T = 200(2)$ K, triclinic, space group $P\bar{1}$, $a = 13.0638(3)$, $b = 13.8907(3)$, $c = 20.4848(4)$ Å, $\alpha = 83.4710(10)$, $\beta = 80.8050(10)$, $\gamma = 81.6320(10)°$, $V = 3614.85(13)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.463$ Mg m^{-3}, $\mu = 1.495$ mm^{-1}, reflections collected: 31215, independent reflections: 12664 ($R_{int} = 0.0340$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0408$, $wR_2 = 0.1106$, R indices (all data): $R_1 = 0.0599$, $wR_2 = 0.1198$; **11**: $C_{54}H_{76}Cl_2Mo_2N_4O_2$, $M_r = 1075.97$, $T = 200(2)$ K, triclinic, space group $P\bar{1}$, $a = 10.6576(16)$, $b = 13.8872(13)$, $c = 19.530(3)$ Å, $\alpha = 84.958(4)$, $\beta = 75.534(6)$, $\gamma = 73.552(5)°$, $V = 2683.9(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.331$ Mg·m^{-3}, $\mu = 0.609$ mm^{-1}, reflections collected: 23358, independent reflections: 9395 ($R_{int} = 0.0936$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0661$, $wR_2 = 0.1461$, R indices (all data): $R_1 = 0.1355$, $wR_2 = 0.2156$; **12**·2.9 OEt_2: $C_{75.60}H_{111}Cl_2Mo_2N_4O_{4.90}$: $M_r = 1417.06$, $T = 200(2)$ K, triclinic, space group $P\bar{1}$, $a = 13.0258(19)$, $b = 14.299(2)$, $c = 19.963(3)$ Å, $\alpha = 83.341(2)$, $\beta = 80.195(2)$, $\gamma = 80.632(2)°$, $V = 3600.1(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.307$ Mg m^{-3}, $\mu = 0.466$ mm^{-1}, reflections collected: 29223, independent reflections: 12601 ($R_{int} = 0.0294$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0466$, $wR_2 = 0.1463$, R indices (all data): $R_1 = 0.0555$, $wR_2 = 0.1533$; **13**·0.5 OEt_2: $C_{67.5}H_{88}Cl_2Mo_2N_4O_2$: $M_r = 1250.20$, $T = 200(2)$ K, monoclinic, space group $P\bar{1}$, $a = 11.9353(12)$, $b = 12.8026(12)$, $c = 23.213(2)$ Å, $\alpha = 83.4280(10)$, $\beta = 84.3730(10)$, $\gamma = 75.2160(10)°$, $V = 3398.3(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.222$ Mg m^{-3}, $\mu = 0.490$ mm^{-1}, reflections collected: 28012, independent reflections: 11907 ($R_{int} = 0.0355$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0554$, $wR_2 = 0.1450$, R indices (all data): $R_1 = 0.0783$, $wR_2 = 0.1542$; (**14** + **15**)·4.5 OEt_2: $C_{82}H_{125}BrClMo_2N_4O_{6.50}$: $M_r = 1578.10$, $T = 200(2)$ K, triclinic, space group $P\bar{1}$, $a = 12.920(6)$, $b = 13.905(6)$, $c = 20.310(10)$ Å, $\alpha = 83.858(8)$, $\beta = 80.605(7)$, $\gamma = 82.704(11)°$, $V = 3557(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.474$ Mg m^{-3}, $\mu = 1.012$ mm^{-1}, reflections collected: 29458, independent reflections: 12546 ($R_{int} = 0.0773$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0729$, $wR_2 = 0.2006$, R indices (all data): $R_1 = 0.1345$, $wR_2 = 0.2227$. CCDC 922848 (**4**), CCDC 922849 (**5**), CCDC 929100 (**7**), CCDC 922846 (**9**·2.7 C_5H_{12}), CCDC 922847 (**10**·4.1 OEt_2), CCDC 941798 (**11**), CCDC 922850 (**12**·2.9 OEt_2), CCDC 922851 (**13**·0.5 OEt_2), CCDC 922852 ((**14** + **15**)·4.5 OEt_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.cam.ac.uk/data_request/cif.

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