Ternary Alkali Metal Transition Metal Acetylides A_2MC_2 (A = Na, K; M = Pd, Pt)

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 65th birthday

Abstract: Ternary transition metal acetylides A_2MC_2 (A = Na, K; M = Pd, Pt) can be synthesised by reaction of the respective alkali metal acetylide A_2C_2 with palladium or platinum in an inert atmosphere at about 350 °C. The crystal structures are characterised by $_\infty^1[M(C_2)_{2/2}^{2-}]$ chains, which are separated by the alkali metals ($P\bar{3}m1$, $Z = 1$). The refinement of neutron powder diffraction data gave C–C = 1.263(3) Å for Na_2PdC_2 (Na_2PtC_2: 1.289(4) Å), which is distinctively longer than the expected value for a C–C triple bond (1.20 Å). On the basis of band-structure calculations this can be attributed to a strong back-bonding from the metal into the antibonding orbitals of the C_2 unit. This was further confirmed by Raman spectroscopic investigations, which showed that the wavenumbers of the C–C stretching vibrations in Na_2PdC_2 and Na_2PtC_2 are about 100 cm^{-1} smaller than in acetylene. ^{13}C MAS-NMR spectra demonstrated that the acetylenic C_2 units in the title compounds are very different from those in acetylene. Electrical conductivity measurements and band-structure calculations showed that the black title compounds are semiconductors with a small indirect band gap (approximately 0.2 eV).

Keywords: acetylides · alkali metals · neutron diffraction · palladium · platinum

Introduction

When in 1997 we showed that ternary alkali metal transition metal acetylides are accessible by the reaction of Na_2C_2 with palladium or platinum, these black compounds were the first structurally characterised examples of their class.[1] Solution and refinement of their crystal structures from X-ray powder diffraction data showed that $_\infty^1[M(C_2)_{2/2}^{2-}]$ chains (M = Pd, Pt) are the characteristic structural feature. The only other details we gave at that time were that the stretching frequency of the C–C bond was about 100 cm^{-1} lower than that of acetylene[2] and that the measured diamagnetic behaviour was consistent with the presence of Pd^0. Since then we have found another synthetic route to alkali metal transition metal acetylides AM^IC_2 (A = alkali metal; M^I = Cu,[3, 4] Ag,[5] Au[6]) by heating complex ternary hydrogen acetylides obtained in liquid ammonia. These compounds are colourless to yellow and exhibit typical salt-like properties. As the different colours indicated differing properties of the ternary acetylides AM^IC_2 and Na_2MC_2, we investigated Na_2PdC_2 and Na_2PtC_2 in more detail. The results of neutron diffraction experiments, spectroscopic investigations (Raman, ^{13}C MAS-NMR) and measurements of the electrical conductivity are reported herein and discussed on the basis of theoretical band-structure calculations. The new compounds K_2PdC_2 and K_2PtC_2, which are isotypic with Na_2PdC_2 and Na_2PtC_2, are also presented.

Results and Discussion

Na_2PdC_2 and Na_2PtC_2 can be synthesised by the reaction of Na_2C_2[7–9] with palladium or platinum in an argon atmosphere.[1] By the use of K_2C_2[7, 9] this procedure has been extended to the synthesis of K_2PdC_2 and K_2PtC_2 under analogous conditions (see Experimental Section). All the

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compounds were black, polycrystalline and sensitive to air and moisture. With a slight surplus of the alkali metal, acetylide products free of impurities detectable by X-ray powder diffraction could be obtained, but neutron diffraction and ^{13}C MAS-NMR experiments revealed that smaller amounts of the starting materials were still present (vide infra). With a higher surplus of the alkali metal acetylide the unreacted binary acetylides were detectable by X-ray powder diffraction; a surplus of palladium or platinum led to PdC_x[10] or unreacted platinum, respectively.

The evolution of the reaction could be monitored on a high-temperature X-ray powder diffractometer by heating the starting materials sealed in a capillary under argon. The reaction of Na_2C_2 with palladium in the range 50–550 °C (Figure 1) started at about 280 °C and was almost complete at about 400 °C. No intermediate products were visible in the diffraction patterns. Similar reaction temperatures were found for the other title compounds.

No comparable reaction of Na_2C_2 or K_2C_2 with nickel was observed. Only Ni_3C[11] could be obtained as a reaction product. Similarly, the reaction of Li_2C_2[12, 13] with nickel, palladium or platinum was unsuccessful: only known intermetallic lithium compounds were formed.[14]

The crystal structures of Na_2PdC_2 and Na_2PtC_2 had already been solved and refined from X-ray powder diffraction data.[1] K_2PdC_2 and K_2PtC_2 are isotypic with the sodium compounds; the lattice parameters and some details of the X-ray powder investigations are summarised in Table 1.

The *c* axis is almost independent of the respective alkali metal; this indicates a structural motif along this direction which consists solely of carbon and the transition metal. Indeed, in the resulting crystal structure (Figure 2) $^1_\infty[M(C_2)^{2-}_{2/2}]$ chains running along the crystallographic *c* axis are the characteristic structural feature. These chains are separated by the alkali metals, which show an unusual coordination, with three C atoms at a short distance and three transition metals at a slightly longer distance, so that a very distorted trigonal prism results. In the chains each transition metal is coordinated by two C_2 dumbbells in an *end-*

Abstract in German: *Ternäre Übergangsmetallacetylide der Zusammensetzung A_2MC_2 (A = Na, K; M = Pd, Pt) können durch Reaktion der entsprechenden Alkalimetallacetylide A_2C_2 mit Palladium oder Platin in einer inerten Atmosphäre bei ca. 350 °C dargestellt werden. Die Kristallstrukturen sind durch $^1_\infty[M(C_2)^{2-}_{2/2}]$-Ketten charakterisiert, die durch die Alkalimetallionen separiert werden ($P\bar{3}m1$, Z = 1). Auf Grundlage von Neutronenbeugungsuntersuchungen wurde für Na_2PdC_2 ein C-C-Abstand von 1.263(3) Å erhalten (Na_2PtC_2: 1.289(4) Å), der deutlich größer ist als der Erwartungswert für eine C–C-Dreifachbindung (1.20 Å). Basierend auf Bandstrukturrechnungen kann dies auf starke Rückbindungen vom Metall in die antibindenden Orbitale der C_2-Einheit zurückgeführt werden. Dies wird ferner durch die Ergebnisse von ramanspektroskopischen Untersuchungen bestätigt, bei denen gefunden wurde, daß die Wellenzahl der C–C-Streckschwingung in Na_2PdC_2 und Na_2PtC_2 um ca. 100 cm^{-1} kleiner ist als in Acetylen. Ferner zeigen ^{13}C MAS-NMR-Untersuchungen, daß sich die acetylidischen C_2-Einheiten in den ternären Übergangsmetallacetyliden deutlich von denen in Acetylen unterscheiden. Weiterhin ergaben Messungen der elektrischen Leitfähigkeiten und Bandstrukturrechnungen, daß die schwarzen Titelverbindungen Halbleiter mit einer sehr kleinen indirekten Bandlücke von ca. 0.2 eV sind.*

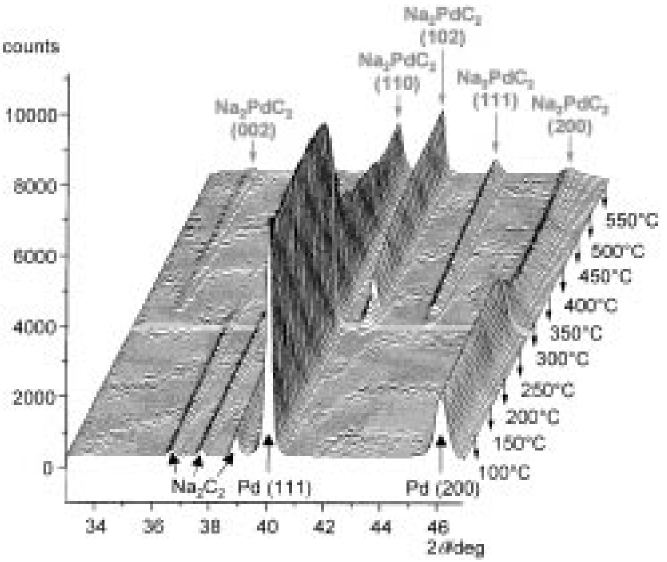

Figure 1. Formation of Na_2PdC_2 from Na_2C_2 and palladium with increasing temperature as measured on an X-ray powder diffractometer (Huber G644). The reflection assignments and the starting temperature of the reaction are highlighted.

Table 1. Selected crystallographic data (STOE Stadi P2, 298 K) of ternary palladium and platinum acetylides ($P\bar{3}m1$, $Z = 1$).

	Na_2PdC_2	Na_2PtC_2	K_2PdC_2	K_2PtC_2
a [Å]	4.4638(1)	4.5031(3)	5.1033(2)	5.1218(1)
c [Å]	5.2668(2)	5.2050(5)	5.2828(2)	5.2179(1)
V [Å^3]	90.883(7)	91.40(1)	119.150(9)	118.539(7)
wR_P	0.0430	0.0450	0.0343	0.0412
R_P	0.0338	0.0359	0.0262	0.0319
R_{Bragg}	0.0623	0.0391	0.0691	0.0290
No. of reflections	39	50	63	67
2*θ* range [°]	15–90	16–100	16–100	16–105

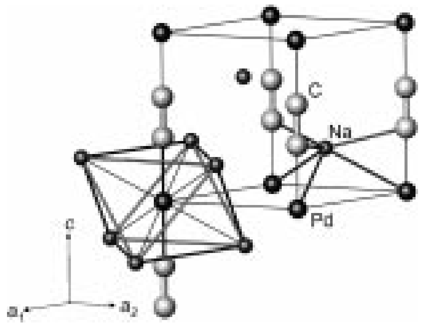

Figure 2. Crystal structure of Na_2PdC_2. The unit cell, the C–C bonds, the distorted trigonal prismatic surroundings of one Na atom, the linear carbon coordination and the octahedral Na surroundings of one Pd atom are emphasised.

on fashion, and vice versa. The linear coordination of the transition metal is in good agreement with the expected coordination of Pd^0 or Pt^0 with a d^{10} electron configuration.

To obtain reliable atomic parameters for the light atoms (sodium and carbon) and thus accurate bond lengths in the transition metal carbon chains, neutron diffraction experiments were performed on Na_2PdC_2 and Na_2PtC_2 (see Experimental Section). Some resulting interatomic distances are given in Table 2. The quality of the data and the refinement can be estimated from the example in Figure 3.

Table 2. Selected interatomic distances [Å] of Na_2PdC_2 and Na_2PtC_2.

	Na_2PdC_2	Na_2PtC_2
Pd/Pt–C	2.002(2) 2 ×	1.958(2) 2 ×
Na–Pd/Pt	2.968(2) 3 ×	2.967(3) 3 ×
Na–C	2.631(1) 3 × 3.139(3) 3 ×	2.652(1) 3 × 3.170(3) 3 ×
C–C	1.263(3)	1.289(4)

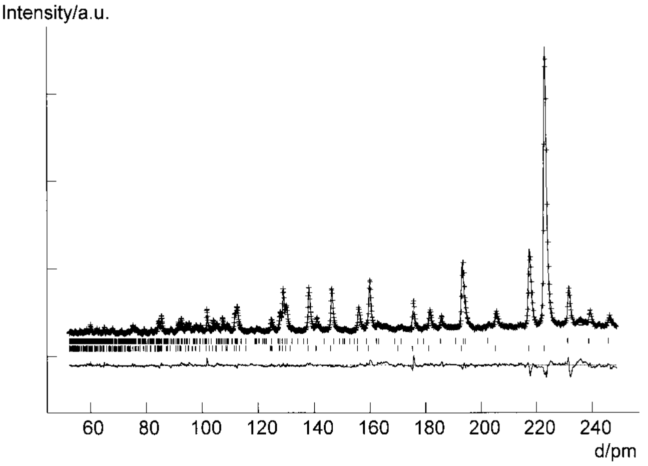

Figure 3. Neutron diffraction time-of-flight pattern (backscattering) of Na_2PdC_2 at 298 K, showing the observed (+) and calculated patterns (solid line) as well as the difference between them. Vertical bars mark the positions of the reflections of Na_2C_2 (upper bars) and Na_2PdC_2 (lower bars).

Among the interatomic distances in Table 2, the C–C bond lengths are the most remarkable, since they deviate from the expected value for a C–C triple bond (1.20 Å[15]) by more than 0.06 Å. This is discussed in more detail at the end of this contribution. The Na–C distances are in good agreement with the values found for Na_2C_2 (2.617(4)–2.798(4) 6 ×).[9] The sample investigated by neutron diffraction contained small amounts of Na_2C_2, which could not be detected by X-ray powder diffraction (Figure 3). This is discussed in more detail with the ^{13}C NMR results below.

Another interesting feature is the temperature dependence of the lattice parameters of Na_2PdC_2 and Na_2PtC_2 measured between 10 and 298 K. The value of a increases, as expected, with increasing temperature (Na_2PdC_2: $a = 4.4375(9)$ Å at 10 K, 4.4638(1) Å at 298 K; Na_2PtC_2: $a = 4.484(1)$ Å at 10 K, 4.5031(3) Å at 298 K), whereas c decreases slightly (Na_2PdC_2: $c = 5.275(1)$ Å at 10 K, 5.2668(2) Å at 298 K; Na_2PtC_2: $c = 5.216(1)$ Å at 10 K, 5.2050(5) Å at 298 K). This points to an increasing librational motion of the C_2 dumbbells around their centre of gravity with increasing temperature which affects the a axis (perpendicular to the dumbbell axis) more than the c axis (parallel to the dumbbell axis). This effect is also well known for several binary alkali metal and alkaline earth metal acetylides.[16]

For the platinum compounds c is always about 0.06 Å less than c for the respective palladium compounds (see Table 1). This difference may be attributed to relativistic effects,[17] which should peak at the pair Ag–Au. Indeed, in $AAgC_2$[5] and $AAuC_2$[6] (A = Li–Cs) with similar chain structures c differs by more than 0.1 Å ($LiAgC_2$: $c = 5.328(3)$ Å; $LiAuC_2$: $c = 5.194(7)$ Å; both compounds crystallise in isotypic structures with $^1_\infty[M(C_2)^-_{2/2}]$ chains).

^{13}C MAS-NMR spectroscopy is a very useful tool for characterising metal acetylides.[9, 18–20] The ^{13}C NMR spectroscopic parameters of Na_2C_2 and K_2C_2[9] can be compared with those of the new ternary palladium and platinum compounds (see Experimental Section and Figure 4).

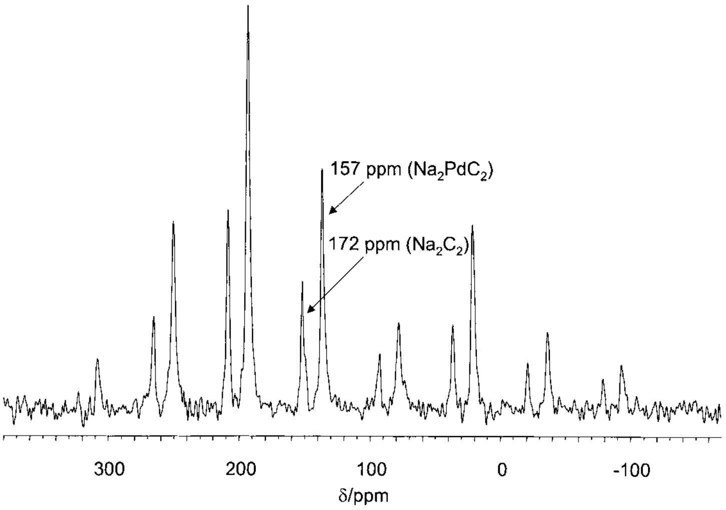

Figure 4. ^{13}C MAS-NMR spectrum of Na_2PdC_2: the centre bands at the isotropic chemical shifts of Na_2C_2 and Na_2PdC_2 are marked. MAS frequency 4320 Hz, π/2 pulse length 5 µs, 520 scans, time between RF pulses 180 s.

It is surprising that two sets of resonance lines were observed, as the structure of Na_2PdC_2 contains only one crystallographically independent carbon atom, but comparison with the spectrum of Na_2C_2[9] makes it clear that the smaller signal must be assigned to the unreacted starting material, Na_2C_2. Therefore, contrary to the results of X-ray powder diffraction, the product is not free of impurities. Na_2C_2 contains only light elements which are almost invisible in the X-ray powder diffraction patterns. With methods such as ^{13}C NMR spectroscopy or neutron powder diffraction, however, these impurities can be detected.

The spectra obtained for Na_2PdC_2 and K_2PdC_2 were analysed for the intensities of their spinning side bands to determine the shielding parameters (see Experimental Section),[21] which are summarised and compared with those obtained for Na_2C_2, K_2C_2 and solid C_2H_2[22] in Table 3 (for Na_2PtC_2 and K_2PtC_2 the poor quality of the spectra did not allow an analysis of the spinning side bands).

Table 3. ^{13}C MAS-NMR parameters of binary and ternary acetylides and solid acetylene.

	δ_{iso} [ppm][a]	$\Delta\sigma$ [ppm][b]	η[c]
Na_2PdC_2	157	359	0.20
Na_2PtC_2	156	–[d]	–[d]
K_2PdC_2	162	317	0.15
K_2PtC_2	162	–[d]	–[d]
Na_2C_2[9]	172	342	0.17
K_2C_2[9]	186	285	0.15
C_2H_2[22]	70	240	0

[a] Isotropic chemical shift (relative to external $(CH_3)_4Si$): $\delta_{iso} = -\sigma_{iso} = -1/3(\sigma_{11}+\sigma_{22}+\sigma_{33})$ with $|\sigma_{33}-\sigma_{iso}| \geq |\sigma_{11}-\sigma_{iso}| \geq |\sigma_{22}-\sigma_{iso}|$; $\Delta(\delta_{iso}) \leq \pm 1$ ppm. [b] Shielding anisotropy: $\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11}+\sigma_{22})$; $\Delta(\Delta\sigma) \leq \pm 5$ ppm (for K_2PdC_2: ± 10 ppm). [c] Asymmetry parameter: $\eta = 3/2(\sigma_{22}-\sigma_{11})/\Delta\sigma$; $\Delta(\eta) \leq \pm 0.05$. [d] Not determined.

The isotropic chemical shifts of the binary and ternary acetylides are similar, but they are markedly different from that of acetylene. The deshielding of the binary acetylides is slightly greater than that of the ternary transition metal acetylides and increases as the number of electrons on the alkali metal rises. The latter effect is also found for the ternary acetylides, but it is less pronounced. The shielding anisotropy $\Delta\sigma$, however, decreases with an increasing number of electrons. By far the smallest value of $\Delta\sigma$ was found for acetylene. For an ideal axial symmetric environment around the C atoms the asymmetry parameter η should be zero. Consistently with the lack of axial symmetry around the C_2 dumbbells in the given crystal structures, it was found that the asymmetry parameters are significantly different from zero. The difference between the components of the shielding tensor in the plane perpendicular to the dumbbell axis amounts to at least 30 ppm. For acetylene frozen in an argon matrix[22] an asymmetry parameter of zero was obtained, which is in agreement with the point symmetry of the C_2H_2 molecule.

To summarise the findings of the ^{13}C NMR experiments: the NMR parameters of the binary and ternary acetylides are comparable, but they differ very much from those of acetylene; furthermore, the influence of the alkali metal ion on the NMR parameters is stronger in the binary acetylides than in the ternary compounds.

The magnetic susceptibilities of A_2MC_2 (A = Na, K; M = Pd, Pt) were measured on a Squid magnetometer in the temperature range 1.7–298 K with applied magnetic fields of up to 5 T. As expected for compounds with transition metals in a d^{10} electron configuration, temperature-independent diamagnetic behaviour was observed. Only below 20 K was a slight increase in the magnetic susceptibilities obtained, probably due to small amounts of unknown paramagnetic impurities.

Agreement between the mean values of the susceptibilities observed between 100 and 298 K and the theoretical values calculated from the respective diamagnetic increments[23, 24] (Table 4) is excellent for Na_2PdC_2 and K_2PtC_2 and reasonable for the other two compounds.

The black colour of the title compounds suggested that they are conductors or semiconductors. When their electrical conductivity was measured by using a PPMS system (Quantum Design; see Experimental Section), all four compounds showed the typical behaviour of a semiconductor, namely, decreasing resistivity with increasing temperature; an example is shown in Figure 5. As the expected linear behaviour is not observed in the $\ln(1/R) = f(1/T)$ plot, it must be assumed that two different conduction mechanisms exist. We suggest that, as for many similar systems, at low temperatures the conduction is mainly affected by defects, whereas at higher temperatures the intrinsic conduction mechanism gains the upper hand. The most linear behaviour was observed in the $\ln(1/R) = f(1/T)$ plot of K_2PtC_2. The activation energy (that is, the band gap) from the high-temperature data was estimated to be $E_A \approx 0.18$ eV, a value comparable with the band gap obtained from band-structure calculations on Na_2PdC_2 using the LMTO (linear muffin-tin orbitals) method within density functional theory (see Experimental Section).[25, 26]

Table 4. Mean values of magnetic susceptibilities of ternary palladium and platinum acetylides measured in the range 100–298 K and comparison with theoretical values calculated using diamagnetic increments.

	χ_{mol}(meas.) [10^{-11} m^{3}mol^{-1}]	χ_{mol}(calcd) [10^{-11} m^{3}mol^{-1}]
Na_2PdC_2	−76	−76
Na_2PtC_2	−79	−99
K_2PdC_2	−124	−96
K_2PtC_2	−121	−119

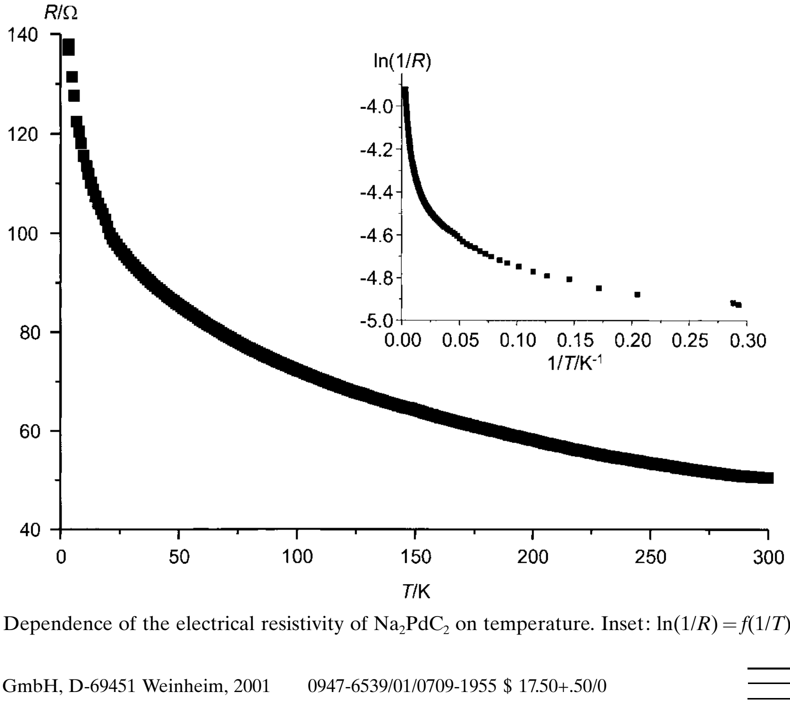

Figure 5. Dependence of the electrical resistivity of Na_2PdC_2 on temperature. Inset: $\ln(1/R) = f(1/T)$.

Figure 6 shows that Na_2PdC_2 is a semiconductor with a small indirect band gap (highlighted) of about 0.2 eV. For the calculations the structural data of the neutron diffraction experiments were used with the lattice parameters of the low-temperature X-ray investigations taken at 10 K (see above). Density functional calculations typically provide band gaps which are smaller than the experimental value,[27] but this calculated value for Na_2PdC_2 is in good agreement with the estimated experimental band gap for K_2PtC_2.

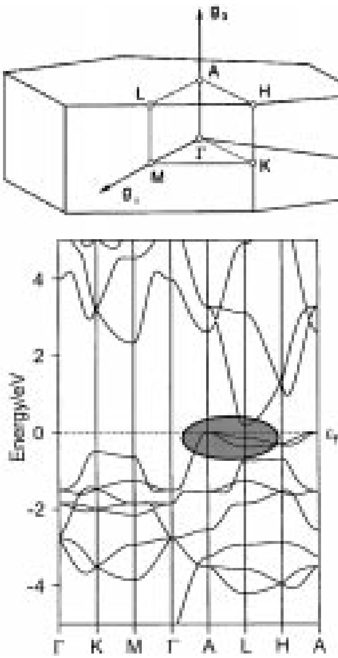

Figure 6. Band structure of Na_2PdC_2. The Fermi level was chosen as the zero-point energy. The indirect band gap is highlighted.

The band structure of Na_2PtC_2 looks very similar to that in Figure 6, but the band gap is even smaller. Unfortunately, the quantitative analysis of the electrical conductivity measurements is not good enough to be compared with the results of the band-structure calculations. No band structures were calculated for K_2PdC_2 and K_2PtC_2, as no reliable atomic parameters were available from neutron diffraction investigations.

The conduction band of Na_2PdC_2 between the points A and L of the Brillouin zone, which is along the zone edge in the *a*,b** plane, shows a surprisingly large band width which was deduced, from a fat-band analysis, to consist mainly of contributions from Na 3s and C $p_{x,y}$ orbitals, the latter having a π antibonding character. A more detailed analysis showed that Na–C interactions are weakly antibonding at A and bonding at L, and the change between antibonding and bonding behaviour leads to the observed large band width of the conduction band between these points. Furthermore, calculations with different C–C distances showed that shorter distances lead to a smaller band width of the conduction band between A and L and thus a larger band gap. It is surprising that $CsAgC_2$, which has a similar crystal structure with ${}^1_\infty[\mathrm{Ag}(C_2)^-_{2/2}]$ chains separated by the cesium atoms, is colourless and shows insulating behaviour (vide infra). It would therefore be interesting to synthesise and analyse the electronic properties of compounds such as $A^{II}MC_2$ (A^{II} = alkaline earth metal; M = Pd, Pt). The electronic situation should be comparable with that of Na_2PdC_2, but the crystal structure should be similar to that of $CsAgC_2$. Unfortunately, our experiments in these systems, especially the reaction of MgC_2[28, 29] with palladium or platinum, have not yet been successful and have led to new, probably intermetallic, phases.[30]

Vibrational spectroscopy was shown to be a helpful tool for characterising the bonding in, for example, carbonyl complexes, from the frequency of the C–O stretching vibration.[31] As the C_2 units are symmetrically surrounded in binary and ternary acetylides, Raman spectroscopy has to be used to obtain the frequencies of the C–C stretching vibrations, which may well yield useful information about the bonding in these compounds.

Several trends are evident in Table 5. The wavenumbers of the C–C stretching vibration in binary alkali metal acetylides and ternary palladium and platinum acetylides are very similar to each other, but they differ by approximately 100 cm^{-1} from that of acetylene, which, however, compares quite well with the wavenumbers in ternary silver and gold acetylides. The difference between the silver and palladium acetylides is explained below. Furthermore, the decrease in the wavenumbers of the C–C stretching vibration with an increasing number of electrons on the alkali metal is clear for the binary acetylides, less pronounced for the palladium and platinum compounds and negligible for the silver and gold acetylides. At least for the binary acetylides, this is probably attributable to a decreasing electronegativity from sodium to potassium, which leads to a higher negative charge on the C_2 dumbbell, which affects the C–C stretching vibration as described.[32] This effect seems to be less important in the ternary compounds.

Table 5. Raman spectroscopy: wavenumbers [cm^{-1}] of C–C stretching vibrations ($\tilde{\nu}_{C\equiv C}$) of binary and ternary acetylides.

	A_2C_2	A_2PdC_2	A_2PtC_2	$AAgC_2$	$AAuC_2$
A = Na	1845[9]	1862	1845	1965[5]	1997[6]
A = K	1821[9]	1850	1840	1963[5]	1997[6]
A = H	1974[2]				

Whereas Na_2PdC_2 and the other title compounds are black and show semiconducting behaviour, $CsAgC_2$ and related ternary acetylides with comparable ${}^1_\infty[\mathrm{M^I}(C_2)^-_{2/2}]$ chain structures (M^I = Cu, Ag, Au)[4–6] are almost colourless and act as insulators, as mentioned above. Among the properties of Na_2PdC_2 and $CsAgC_2$,[5] as typical examples of these classes of compounds, summarised in Table 6, the most interesting is the C–C bond length, which is in the range expected for a C–C triple bond in $CsAgC_2$, but it is more than 0.06 Å longer in Na_2PdC_2. We think that a stronger backbonding from palladium into the antibonding orbitals of the C_2 unit is responsible for this increase in the C–C bond length, which is also demonstrated by a decrease in the respective C–C

Table 6. Comparison of some properties of Na_2PdC_2 and $CsAgC_2$.[5]

	Na_2PdC_2	$CsAgC_2$
C–C [Å]	1.263(3)	1.217(7)
M–C [Å] (M = Pd, Ag)	2.002(2)	2.015(4)
sum radii M–C [Å]	2.06	2.03
colour	black	colourless
conductivity	semiconductor	insulator
$\tilde{\nu}_{C\equiv C}$ [cm^{-1}]	1862	1965
iCOHP(M–C(π)) [eV per bond]	0.24	0.06

stretching vibration. This is confirmed by a comparison of the calculated bond length for an M–C bond from theoretical radii[15] with the experimental value: the latter is much shorter than the theoretical value for the Pd–C distance in Na_2PdC_2, whereas in $CsAgC_2$ there is only a small difference between these two values. Therefore the bonding can be represented simply by the electron–dot structures in Equation (1), [33] in which the left-hand structure describes more or less the bonding in $CsAgC_2$, whereas in Na_2PdC_2 the right-hand structure must also be considered.

$$\ldots{-}M{-}C{\equiv}C{-}M{-}\ldots \rightleftharpoons \ldots{=}M{=}C{=}C{=}M{=}\ldots \qquad (1)$$

This is confirmed by analysis of the COHPs (crystal orbital Hamilton populations)[34] of the π-M–C bonding—mainly consisting of overlaps of the metal d–π orbitals with carbon p–π orbitals—in the band structures of Na_2PdC_2 and $CsAgC_2$. The higher integrated value (iCOHP) for Na_2PdC_2 (Table 6) indicates a stronger backbonding in this compound.

Currently we are investigating the kinetics of the reaction of Na_2C_2 with palladium by diffraction methods. We have found that an increase in the reaction temperature of about 20 K increases the reaction time by a factor of 10. Furthermore we were able to synthesise Rb_2MC_2 and Cs_2MC_2 (M = Pd, Pt) by analogous reactions. This will be the subject of a forthcoming contribution.[35]

Experimental Section

Preparation of compounds: The title compounds were prepared by reaction of the respective alkali metal acetylide with palladium (Alfa, 99.9985 %) or platinum (ABCR, 99.9 %) powder in an inert atmosphere at about 350 °C. Na_2C_2 and K_2C_2 were synthesised according to the procedures given in the literature[9] and their purity was checked by X-ray powder diffraction. In a typical experiment, the alkali metal acetylide (1.2 mmol) and the transition metal (1 mmol) were mixed in a glove-box (argon atmosphere) and pressed to pellets (∅ = 10 mm), which were transferred in a corundum crucible into a horizontal tube furnace, where they were heated to 350 °C in an argon atmosphere for about 15 h. The products were allowed to cool and transferred back to the glove-box, where all further handling was carried out. The resulting powders were black and sensitive to air and moisture.

Crystal structure determinations: Room-temperature X-ray powder diffraction was carried out on a STOE Stadi P2 powder diffractometer (Ge monochromator, $Cu_{K\alpha 1}$ radiation, linear position-sensitive OED detector). The samples were measured in capillaries (∅ = 0.3 mm) sealed in an argon atmosphere.

For the low-temperature investigations a Huber G645 powder diffractometer was used ($Cu_{K\alpha 1}$ radiation, Ge monochromator, scintillation counter, closed-cycle He cryostat). The samples were measured on a flat sample holder designed for air-sensitive compounds, which was filled in a glove-box.

The high-temperature investigations were carried out on a Huber G644 powder diffractometer (Ge monochromator, $Cu_{K\alpha 1}$ radiation, linear position-sensitive OED detector, Huber furnace). The samples were sealed in capillaries (∅ = 0.3 mm) under argon.

The resulting patterns were indexed using the program TREOR90.[36] A starting model for the structure refinement, guessed from the resulting lattice parameters, was refined by the Rietveld method using *GSAS* software.[37]

The neutron powder diffraction experiments were performed on the Rotax time-of-flight diffractometer[38] at the ISIS spallation source (Rutherford Appleton Laboratory, UK). The samples were measured in vanadium cylinders (∅ = 6 mm, height ≈ 50 mm, wall thickness ≈ 0.1 mm) with aluminium screw caps and air-tight indium seals.

Structure refinement of Na_2PdC_2: Crystal system: trigonal, space group $P\bar{3}m1$ (no. 164), $a = 4.4638(1)$, $c = 5.2658(3)$ Å, $\rho_{calcd} = 3.224$ g cm^{-3}, $Z = 1$, Pd on 1(a), C on 2(c) with $z = 0.3801(3)$, Na on 2(d) with $z = 0.2796(8)$, 32 reflections on the forward- and 282 reflections on the back-scattering bank, five positional and thermal parameters refined, $wR_P = 0.0393/0.0371$, $R_P = 0.0329/0.0342$, $R_{Bragg} = 0.0241/0.1213$; the investigated sample contained 8.5(2) wt % Na_2C_2.

Structure refinement of Na_2PtC_2: Crystal system: trigonal, space group $P\bar{3}m1$ (no. 164), $a = 4.5013(1)$, $c = 5.2047(3)$ Å, $\rho_{calcd} = 4.819$ g cm^{-3}, $Z = 1$, Pt on 1(a), C on 2(c) with $z = 0.3762(4)$, Na on 2(d) with $z = 0.275(1)$, 117 reflections on the forward- and 113 reflections on the back-scattering bank, five positional and thermal parameters refined, $wR_P = 0.0376/0.0506$, $R_P = 0.0299/0.0413$, $R_{Bragg} = 0.0331/0.0258$; the investigated sample contained 14.6(3) wt % Pt and 7.8(1) wt % Na_2C_2.

All refinements were carried out with the GSAS suite of programs.[37]

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-411388 (Na_2PdC_2) and CSD-411389 (Na_2PtC_2).

NMR spectroscopy: The solid-state ^{13}C MAS-NMR spectra were recorded at a resonance frequency of 75.5 MHz on a Bruker AC300 spectrometer with an additional high-power unit and a 7 mm MAS probe. In a glove-box, the samples were placed in air-tight rotors with Teflon caps. The spinning side-band intensities were analysed with the Bruker WIN-FIT program.[39]

Magnetic and electrical property determinations: The magnetic susceptibilities were measured with a Squid MPMS-5S (Quantum Design). The powdered samples were sealed in a quartz capillary (∅ = 2 mm; sample fixed with a quartz sphere) under argon. The measured susceptibilities were corrected for the diamagnetic contributions from the quartz capillary and the quartz sphere. Measurements at five different magnetic fields revealed that all the samples contained only minor amounts of ferromagnetic impurities.

Electrical conductivity measurements were conducted on a PPMS (Quantum Design) in the range 3.5–298 K. The ground sample (approximately 250 mg) was pressed with four copper wires (∅ = 0.3 mm) to a powder pellet (∅ = 12 mm, height ≈ 1 mm). The copper wires were arranged in a linear way, so no quantitative analysis could be performed.

Calculations: For electronic band-structure calculations, the LMTO method[25, 26] within the local density approximation (LDA), taking the von Barth–Hedin approximation, was used.[40] Atomic-sphere radii were chosen by an automated procedure for the TB-LMTO-ASA calculations. Scalar relativistic corrections were included and the calculations were checked for *k*-point convergence.

Raman spectroscopy: The Raman spectra were recorded on a Dilor XY triple spectrometer with an argon laser ($\lambda = 514.5$ nm, 2 mW laser power). The powdered samples were pressed to pellets in a glove-box and transferred into a sample holder designed for measurements on air-sensitive compounds.

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[1] M. Weiß, U. Ruschewitz, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1208.
[2] G. Herzberg, *Molecular Spectra and Molecular Structure*, *Vol. II: Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, **1945**.
[3] R. Nast, *Coord. Chem. Rev.* **1982**, *47*, 89.
[4] U. Cremer, U. Ruschewitz, *Z. Kristallogr.* **2000**, *Suppl. 17*, 128.
[5] W. Kockelmann, U. Ruschewitz, *Angew. Chem.* **1999**, *111*, 3697; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 3492.
[6] J. Offermanns, U. Ruschewitz, C. Kneip, *Z. Anorg. Allg. Chem.* **2000**, *626*, 649.
[7] H. Föppl, *Angew. Chem.* **1958**, *70*, 401.
[8] M. Atoji, *J. Chem. Phys.* **1974**, *60*, 3324.
[9] S. Hemmersbach, B. Zibrowius, U. Ruschewitz, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1440.
[10] G. V. Lisichkin, O. L. Pisarenko, V. Y. Khinchagashvili, M. A. Lunina, *Russ. J. Inorg. Chem.* **1977**, *22*, 619.
[11] S. Nagakura, *J. Phys. Soc. Jpn.* **1958**, *13*, 1005.
[12] R. Juza, V. Wehle, H.-U. Schuster, *Z. Anorg. Allg. Chem.* **1967**, *352*, 252.
[13] U. Ruschewitz, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1599.
[14] P. Villars, L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd ed. (Ed.: W. B. Pearson), ASM International, Materials Park, OH, **1991**.
[15] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.
[16] U. Ruschewitz, *Habilitationsschrift*, RWTH Aachen (Germany), **2000**.
[17] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.
[18] T. M. Duncan, *Inorg. Chem.* **1989**, *28*, 2663.
[19] B. Wrackmeyer, K. Horchler, A. Sebald, L. H. Merwin, C. Ross II, *Angew. Chem.* **1990**, *102*, 821; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 807.
[20] O. Reckeweg, A. Baumann, H. A. Mayer, J. Glaser, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1686.
[21] J. Herzfeld, A. Berger, *J. Chem. Phys.* **1980**, *73*, 6021.
[22] A. J. Beeler, A. M. Orendt, D. M. Grant, P. W. Cutts, J. Michel, K. W. Zilm, J. W. Downing, J. C. Facelli, M. S. Schindler, W. Kutzelnigg, *J. Am. Chem. Soc.* **1984**, *106*, 7672.
[23] W. Haberditzl, *Magnetochemie*, Akademie-Verlag, Berlin, **1968**.
[24] Landolt-Börnstein: *Zahlenwerte und Funktionen aus Naturwissenschaft und Technik*, *Neue Serie*, *Gruppe II: Atom- und Molekularphysik*, *Bd. 2*, *Magnetische Eigenschaften der Koordinations- und Metallorganischen Verbindungen der Übergangselemente*, Springer, Berlin, **1966**.
[25] O. K. Andersen, C. Arcangeli, R. W. Tank, T. Saha-Dasgupta, G. Krier, O. Jepsen, I. Dasgupta, *Tight-Binding Approach to Computational Materials Science*, MRS Symposia Proceedings, no. 491, MRS, Pittsburgh, PA, **1998**.
[26] G. Krier, O. Jepsen, A. Burkhardt, O. K. Andersen, TB-LMTO-ASA program, v. 4.7.
[27] R. O. Jones, O. Gunnarsson, *Rev. Mod. Phys.* **1989**, *61*, 689.
[28] V. Vohn, U. Ruschewitz, *Z. Kristallogr.* **1998**, *Suppl. 15*, 55.
[29] P. Karen, A. Kjekshus, Q. Huang, V. L. Karen, *J. Alloys Compds.* **1999**, *282*, 72.
[30] S. Hemmersbach, *Thesis*, RWTH Aachen (Germany), **1998**.
[31] F. Aubke, H. Willner, *Angew. Chem.* **1997**, *109*, 2506; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2402.
[32] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsspektroskopie*, 2nd ed., Thieme, Stuttgart, **1988**.
[33] R. B. King, *J. Organomet. Chem.* **1997**, *536–537*, 7.
[34] R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* **1993**, *97*, 8617.
[35] U. Ruschewitz, *Z. Anorg. Allg. Chem.*, in press.
[36] P. E. Werner, *Z. Kristallogr.* **1964**, *120*, 375; P. E. Werner, TREOR90, University of Stockholm (Sweden), **1990**.
[37] A. C. Larson, R. B. von Dreele, *Los Alamos Laboratory*, *Rep. no. LA-UR* **1987**, *86*, 748, Los Alamos National Laboratory, Los Alamos, NM; PC version: **1998**.
[38] W. Kockelmann, H. Tietze-Jaensch, E. Jansen, W. Schäfer, *ROTAX Activity Report 95/96*, Rutherford Appleton Laboratory, Chilton, UK, **1997**.
[39] D. Massiot, H. Thiele, A. Germanus, *Bruker Rep.* **1994**, *140*, 43.
[40] U. von Barth, L. Hedin, *J. Phys. C* **1972**, *5*, 1629.

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